THE EFFECTS OF ACID RAIN ON THE MOVEMENT OF IONS IN A TYPIC QUARTZIPSAMMENT SOIL UNDER NATURAL VEGETATION IN FLORIDA

By

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The magnitude of leaching of nutrients from the soil surface to the water table and to a nearby drainage system depends on many factors unique to the site The sensitive deep sands of Florida present an extreme case of low nutrient status and high water flux to great depth In addition, water table characteristics, both physical and chemical, influence the horizontal flow vis-à-vis the vertical flows. Investigations using artificial acid treated irrigation water at pH 3.0, 3.7, and at 4.7 control over a two year period at a lake site in north central Florida suggested a relatively high and rapid loss of nutrients from the soil surface to the water table 4 m below under acid irrigation conditions. Considering the low CEC (3.5 me/100 g), the low base saturation (4%) and the high hydraulic conductivity (74 cm/hr), the implication of effects in the rooting zone of natural vegetation is clear. The magnitude of leaching also depended on the nature of the ion, the depth being considered and the acid treatment. Readsorption of ions in the soil profile was shown to occur. Most of the applied water was lost from the soil site to the water table after 49 hours

Thus plant nutrients could potentially be rapidly and completely lost from the soil. The rate of irrigation application had little effect on the magnitude of ion loss. Lateral movement in the groundwater to the lake likewise was very rapid.

Mounding of water was observed to occur at the water table surface. There was essentially little nonvertical flow to the water table, and horizontal wave movement toward the lake was rapid, despite the essentially flat water table extending more than 50 meters from the lake. The effect of the acid treatments from a very large rain event could be observed chemically and physically in the groundwater near the lake within 24 hours by sampling transect wells.

Laboratory studies on sealed soil columns under saturated water flow conditions at pH 3.0, 3.7, and 4.7 showed ion movement characteristics very similar to those observed in the field. The effect of acid rain was not long lasting and the soils recovered to normal soil leachate chemistry within 96 hours. Calcium was the dominant nutrient in the system and showed the greatest magnitude of loss. Magnesium, however, exhibited the greatest percentage loss from the rooting zone. Potassium showed lower but continual loss. Sulfate adsorption was clearly observed. Aluminum showed increased concentration in soil leachates with the more acid treatments at the 15 cm depth. However, more than 50% of the Al was immobilized at 75 cm depth. Reduction in the percent of the base saturation varied with element and treatment. Total and net elemental losses showed close agreement between field and column studies. Total field losses for the 3.7 pH and 3.0 pH totalled 578 and 297 kg/ha, respectively, with the laboratory showing 655 and 182 kg/ha, respectively. Over a two year period, field losses at 15 and 75 cm were 88% of losses from laboratory column studies.

CHAPTER 1
INTRODUCTION

Acid precipitation is now recognized as a major problem of international dimensions. Although serious ecological impacts of the phenomenon are commonly thought to be a problem and product of the industrial north, recent studies have demonstrated the occurrence of acid rain in such diverse areas as California, the Pacific Northwest, Colorado, and Florida. The phenomenon is of special interest to Florida. The soils of northern and central Florida are very sandy and lack significant buffering capacities. Soft-water lakes that occupy shallow depressions in sand hills reflect the characteristics of the soils and are low in buffering capacity. Thus both terrestrial and aquatic ecosystems in northern and central Florida are highly susceptible to acidification from atmospheric inputs. Several recent surveys (e.g., McFee, 1980, Klopatek at al., 1980) have recognized parts of northern Florida to be highly sensitive toward the affects of acid precipitation. Florida is also one of the most rapidly growing states in terms of population. Since the acidity of Florida rainfall has been shown to be derived primarily from in-state emissions of SO_2 and NO_x (Brezonik et al., 1981), the demographic trends imply that acidic emissions, and hence acid precipitation, are likely to increase in intensity over the coming decades. This trend is compounded by both the switch from oil-fired and natural gas-fired power plants to coal-fired plants and the increasing tendency to construct power plants inland, rather than at coastal locations. Acid precipitation is also of special interest in Florida because the economy of the state is tied closely to tourism and recreational activities.

Soils that are considered to be most sensitive have low cation exchange capacities (below 5 meq/100 g), low fertility status, pH's above 5, and no free $CaCO_3$. This soil description fits a relatively important group of soils in Florida and surrounding southeastern states. For example, the largest acreage of citrus production in Florida is on the "sand hills of central Florida." It is estimated that 400,000 acres of citrus worth 1/2 billion dollars are produced on soils of this type. Acid precipitation could remove significant quantities of bases from these soils.

The second largest potentially damaging effect of acid precipitation on Florida soils would be in the area of forestry. The timber industry in Florida is largely located in the central to northern sections of the state. At the present time, most forest production is on flatwoods soils (spodosols), however, the industry is strongly considering expansion of tree plantings to sand hills. Since the sandhill soils have lower native fertility and are drier, they have previously been considered uneconomical for forestry production. With higher pressure for forest products, the industry is beginning to use these problem soils. Losses of bases from these soils would be particularly damaging to productivity in that the basic nutrients are not applied in forest production. Declines in productivity would be expected and could be devastating to the wood, pulp, and paper industry.

In addition, newer methods of whole tree harvesting are now being practiced by the forestry industry. This method removes all the aboveground vegetation and thus removes an important recycling component from the system. Large quantities of Ca, Mg, and K which normally are recycled from previously unused plant residues would be lost from the soil. Additional losses of plant nutrients by leaching with acid precipitation would further decrease forest production.

The damage to sand hill lake ecosystems is more obvious. With no external input of bases to these systems, a general nutrient supply depletion and lake acidification will occur. Soil-plant relationships and lake chemistry will be altered.

Acid rain may also lead to alterations of microbiological processes in soils. Those of most concern are N transformation in soils (Alexander, 1980). Much of the data available on the impact of acid rain on soil microbiological processes have been obtained through laboratory studies (Bryant et al., 1979, Strayer and Alexander, 1981). However, little is known about the effects of acid rain on soil microbial activity under field and laboratory conditions. Effects on microbial activity and plant roots are just presently being researched.

Acid precipitation may also affect the aquatic environment. In aquatic systems, acid rain may affect bacteria, phytoplankton, zooplankton, and fish populations as well as an alteration of predator-prey relationships. Lakes may also be subjected to toxic concentrations of Al and other metals leaching from the surrounding watersheds (Cronan and Schofield, 1979, Hendry et al., 1976, Wright and Gjessing, 1976). Thus, the impact of acid precipitation on terrestrial environments may result in chemical and biological alterations. Chemical alterations may consist of leaching of essential alkaline cations with subsequent eventual decrease in soil fertility and productivity as well as release of heavy metals and aluminum impacting groundwater and surface water environments (Babich et al., 1980, Cronan et al., 1978, Wainwright, 1980, Cole and Johnson, 1977, Frink and Voigt, 1977, Meimer, 1976).

Soils have been identified as the "natural integrator" of the effects of acid deposition on terrestrial and aquatic ecosystems. Examination of specific effects of acid deposition on soils is a very complex problem primarily due to the incredibly diverse nature of soils with regard to chemical, physical, and mineralogical properties. The diverse nature of soils has led investigators to look for common denominators among soil properties that will give insight as to short-term as well as long-term effects of acid rain. Soil properties such as pH, base exchange capacity, cation exchange capacity, exchangeable metals, anion sorption capacity (particularly for SO_4), hydraulic conductivity, soil depth, depth to the water table, and type of bedrock are important to any consideration of detrimental effects caused by acid deposition. These parameters are often ranked as to importance by only educated guesses based on data that are usually not directly related to acid deposition. Maps of the U.S. have been developed using these parameters in order to divide landscapes into so-called sensitive or non-sensitive soil areas.

To date, research studies to quantify effects of acid rain on soils are very limited and all suffer from a problem of non-uniform experimental conditions (used by different investigators). Thus comparison of data from different soils is often difficult and differences in observed effects of acid rain may be a result of methodology rather than "true" soil differences. In addition, field and laboratory studies at different locations frequently use different acid rain "formules," different water leaching rates, and certainly different quality control techniques.

Ion-exchange during miscible displacement of acid rain through soil results in a mass transfer of ions between soil colloids and the moving soil solution. This is probably the single most important process influencing the rate of ion migration during water flow through soils. Adsorption (desorption) of one counterion must be accompanied by a stoichiometric desorption (adsorption) of a counterion. Thus, the equilibrium exchange isotherm for an ion in aqueous contact with an exchanger (soil) would depend on the solution concentrations of both the contacting species and the species initially saturating the exchanger. Because these latter cations are metathetically adsorbed (desorbed) during transport of a counterion, they are always present in the transport behavior of the counterion.

Miscible displacement experiments using soil columns have been used successfully to evaluate mobility and sorption-desorption for phosphate, nitrogen, pesticides, and toxic organic compounds for many soils. The technique for acid rain studies would be similar.

Systematic comparisons of a variety of parameters with respect to important physico-chemical parameters including sulfate adsorption ability, exchange capacity, base saturation, permeability, type and percent clay, and organic matter content and extractable acidity are needed. A soil collected with the above parameters in mind would be subjected to acid rain leaching studies at different pH values for the treatments and an acid ratio of 70 30 H_2SO_4:HNO_3 (v/v) including increased simulated canopy throughfall concentrations of other ions. Steady water flux would be maintained for each column A complementary field study of larger scale would provide the natural setting for data collection

Leachates from soil columns and field samplers could be quantified for important ions such as Ca, Mg, Al, SO_4, H, various N forms, and soluble salts. Having properly characterized the soil properties and correlating these with appropriate leachate parameters would allow for calculation of ion mobilities and mass balances.

Thus soils play a key role in ecosystems It is one of their most stable components and, when combined with climate, soils define terrestrial productivity limits and influence aquatic systems directly.

Defining soil sensitivity to acid inputs depends on understanding soil properties and chemistry Thereafter, sensitive soils can be located, the degree of sensitivity determined, and the magnitude of changes in components can be assessed. In addition, the changes are not static but would be expected to be dynamic with time, volume of rain input, and acid concentrations. Thus the sequence of ion losses and adsorption would further characterize the effects of acid precipitation on soils.

Many of the field and laboratory studies are narrow in approach and design and not particularly interrelated A broader ecosystem approach was taken in the field study coupled with a more comprehensive laboratory study, to establish magnitudes of ion losses, sequences of losses, mass balances, rates of losses to the water table, flux characteristics, and rates of movement to lake systems. The main objective was to describe two-dimensional ion mobility as related to inputs, internal processes, and outputs. Specifically, questions concern impacts on soil fertility, nutrient status, toxic substances, plant vitality, and water quality. Both short-term and long-term implications must be considered in relation to numerous soil components, plant-soil relationships, and soil-water relationship (Gorham and McFee, 1980).

The field soil study was one integral part of a terrestrial and aquatic research program, funded by Environmental Protection Agency, Washington, to study the effects of acid precipitation on an ecosystem scale. The main objectives of the study were

1. To examine the effects of acid rain on the movement of ions in a Typic Quartzipsamment soil with respect to time, soil depth, pH treatment, magnitude of ion loss, and sequence of ion loss in field and laboratory column experiments.
2. To quantify sulfate, nitrate, and hydrogen adsorption at two depths in a Typic Quartzipsamment.
3. To examine the effects of acid rain on the chemical properties of soils, including changes in soil nutrient supply and release of potentially toxic ions.
4. To quantify two-dimensional water flow at the field site.
5. To establish rates and magnitude of ion movement to the water table and through the water table towards a lake body.

6. To quantify ion net losses and mass balances in the field and laboratory column experiments and to compare the two approaches for a practical evaluation.

CHAPTER 2
REVIEW OF LITERATURE

Acid Rain: Chemistry and Scope

Although records of rainfall chemistry are not extensive with respect to time, continuous monitoring has revealed the extent of the acid rain problem throughout the world. The European countries such as Norway and Sweden have intensively and for a long period of time obtained records regarding storm movements and acid rain. In North America, rainfall records indicate that whether in Pasadena (Liljestrand and Morgan, 1978), New York (Wolff et al., 1979), or Gainesville, Florida (Hendry and Brezonik, 1980), the pH of the rainfall is about 4.3 (Table 2.1). The industrial northeast, including eastern Canada, is the most seriously acidified area. The acid fringe is moving west and south with pockets in the far west, although the midwest and mountain states are relatively free of acid rain to such a degree.

A review paper by Cogbill and Likens (1974) gave a summary and history of the acid rain problem in the northeast United States. Indeed, the problem is increasing in scope and extent (Wolff et al., 1978). Continuous monitoring at Hubbard Brook Experimental Forest, New Hampshire, showed that the pH frequently fell below pH 4.0 (Eaton et al., 1973).

Table 2.1. Concentration of major ions in rainfall, Gainesville, Florida, 1976-1977

Parameter	Concentration (mg/L)
H	0.0295 (4.53 pH)
TOC	5.20
TON	0.41
NH_4-N	0.10
NO_3-N	0.19
PO_4-P	0.019
total P	0.034
Na	0.44
K	0.20
Ca	0.40
Mg	0.12
Cl	0.98
SO_4	2.05

(Hendry and Brezonik, 1980)

Air-borne substances that influence plants and soils include sea spray, dust (wind, erosion, volcanoes), gases (CO_2, NH_3, SO_2, NO_x), biogenic particles (spores, pollen, hyphal fragments), particulate matter, aerosels and gases (fires, wastes, transportation activities, residential heating, commercial and industrial processing), gases and particulates from the combustion of fossil fuels (Tamm and Cowling, 1975). Proximity to the sea increases Cl, Na, and Mg in rain. In fact, the ratio of Ca:Mg in rain is used as an indicator of source of air-borne substances, being about 0.2 near coastal areas, whereas the continental ratio is much higher, e.g., the Hubbard Brook site is 3.7 (1963-1980 data) (Eaton et al., 1973).

Atmospheric sources of sulfur are burning of fossil fuels, SO_2 abatement, smelters, and fly ash (Terman, 1979). Sulfur is now recognized as the primary source of acidity in rain. The sulfur from the effluent sources is oxidized to sulfur dioxide. During its atmospheric transport, the SO_2 is converted slowly to sulfur trioxide with a conversion rate of from one to several percent per hour, depending on the humidity and other substances in the air. The SO_3 can combine with moisture in the air to form sulfuric acid. The pH of pure air (and water) in equilibrium with carbon dioxide in the air is 5.6 (Shaw, 1977). Data show that SO_2 appears to be having an acidifying effect on grossfall (open rainfall), throughfall, stemflow, and soil solution at sites near major sources. The atmospheric composition of acid rain is generally considered to be 70% sulfuric acid, 23% nitric and 6% hydrochloric acid. The ratios vary, of course, in the eastern U.S. depending on type of industrial source and thus location. The spread and intensification of acid precipitation is attributed to industrial growth downwind from the midwest (Liljestrand and Morgan, 1978).

The strong proton sources in rain are thus H_2SO_4, HNO_3, and HCl with the bound proton sources being H_2CO_3, RCOOH, NH_4, clay, Al, and Fe, the last three only in minute amounts in rain (Galloway et al., 1975). The contribution of free acidity to rain at pH 4.0 is highest for H_2SO_4 at 60 μeq/L, HNO_3 at 34 μeq/L, RCOOH at 6 μeq/L, and all others approaching 0 μeq/L. There are no data on acid rain prior to 1939 nor any synoptic data prior to 1962 in the United States. A single rainstorm was measured in 1939 in Maine and in 1952 Landsberg in Washington measured the pH of rainfall droplets (Likens, 1975). Research on acid rain has only become concentrated since the early 1970s and the first international symposium relating acid rain to the forest ecosystem was as recent as 1975.

It is now obvious that many of the "field" research experiments in eastern North America and western Europe on any aspects of chemistry since the 1950s (which is prior to the records) have been performed under the subtle influence of acid precipitation. This means that there is not a true base for information on which to assess the effects of acid rain over time, but merely a relative scale comparison since acid rain has probably been with us for a long time. This point can be taken further by assuming that the word 'rainfall' is synonymous with "acid rain" since such date indicate that it was present (Likens, 1975).

The impact of acid rain on ecosystems is thus not greatly understood. The potential effects of chronic, long-term exposure of forest soils to acid precipitation have been identified as a major concern since forests are relatively unmanaged (Lee and Weber, 1980).

Any study of the effects of acid rain on soils must consider the differences in quality and quantity between rainfall and the actual input to the soil, the litter leachate (Lee and Weber, 1980). The effects of acid rain on soils indeed can only be adequately studied in an ecosystem context. Specifically, the following must be considered: (1) changes in rain chemistry caused by the passage through canopy and litter layer, (2) effects of soil solution chemistry on uptake of chemicals by plants, (3) effects on biological soil processes, (4) effects on weathering of minerals, and (5) role of hydrogen sulfur and nitrogen on the various pathways in the soil and soil solution.

Feller (1977) demonstrated dramatically the increase in ions as the rain passes via the aqueous route (Table 2 2)

Table 2.2 Average annual cation and anion concentrations in water (mg/L) at several stages during its passage through the ecosystem

Stage	K	Na	Mg	Ca	Fe	Mn	NH_4
Precipitation	0.06	0.30	0.06	0.2	0	0	0.09
Throughfall	1.11	0.64	0.30	1.0	0.01	0.19	0.03
Surface runoff	1.21	0.56	0.39	1.8	0.02	0.17	0.26
Forest floor leachate	1.65	1.04	1.82	2.9	0.39	0.26	0.05
Mineral soil leachate	0.35	0.84	0.65	1.8	0.01	0.01	0.06
Groundwater	0.09	0.87	0.25	1.3	0	0.01	0.02
Streamwater	0.09	1.02	0.31	1.5	0	0	0.02

	Cl	H_2PO_4	NO_3	SO_4	HCO_3	SiO_2
Precipitation	0.6	0.01	0.68	1.3	0.3	0.1
Throughfall	1.7	0.13	1.04	4.9	0.2	0.1
Surface runoff	1.7	0.35	0.58	6.0	1.3	0.5
Forest floor leachate	2.7	0.10	0.18	13.9	6.0	3.7
Mineral soil leachate	1.6	0.03	0.30	5.0	5.0	3.2
Groundwater	0.9	0	0.07	1.7	4.7	2.8
Streamwater	0.8	0.01	0.23	2.1	7.8	4.7

Oxidation and Dynamics of Sulfur Dioxide

The increasing concern about acidic air pollution and acid rain has focused greater attention in recent years on the chemistry of sulfur dioxide which is the major source of acidic air pollution. Its oxidation to sulfate in the atmosphere within the environment of a power plant plume is complicated and is influenced by various factors. Fortunately, the chemistry can be simplified to basic chemical reactions. Models have been developed to predict chemical and physical transformations and the transport of aerosols over great distances under various conditions. Rates of oxidation and nuclei formation, sulfur and particulate dynamics depending on coal or oil sources, the effect of relative humidity, temperature and catalysts, diurnal and seasonal variations, and residence times all affect the formation of acidic sulfate in the atmosphere, as dry deposition and as rain scavenging.

Calvert and Su (1978) made an evaluation of the existing kinetic data related to the elementary, homogeneous reactions of SO_2 within the troposphere. Oxidation of SO_2 can occur at substantial rates through these homogeneous reaction paths. The direct photo-oxidation of SO_2 by way of the electronically excited states of SO_2 is relatively unimportant for most conditions which occur within the troposphere. The oxidation of SO_2 within the natural troposphere is expected to occur largely by way of reactions (1), (2), and (3), with reaction (1) being the dominant path:

(1) $HO + SO_2\ (+M) \longrightarrow HOSO_2\ (+M)$,

(2) $HO_2 + SO_2 \longrightarrow HO + SO_3$,

(3) $CH_3O_2 + SO_2 \longrightarrow CH_3O + SO_3$.

The three reactions occur with about equal rates, SO_2 oxidations can proceed homogeneously at rates as high as 4%/h. Considerations of the reactions in stack gas plumes suggest that a small maximum in the SO_2 photo-oxidation rate may occur during the early stages of the dispersion of a parcel of the stack gases into the air. This should be followed by a short period of slower oxidation. In theory the initial burst is expected to rise from NO_2 and HONO photolysis followed by reaction (1) and the reaction $O(^3P) + SO_2\ (+M) \longrightarrow SO_3\ (+M)$. After the extensive dilution of the stack gases by polluted urban air, the rate of SO_2 homogeneous oxidation is expected to approach that for a typical polluted urban atmosphere (4%/h) (Calvert and Su, 1978)

Atmospheric SO_4 aerosols are believed to be a composite of biogenic and anthropogenic end products, the proportions of which are not known with certainty. The ocean is the only direct source of large quantities of these aerosols. However, these are fairly large particles that have short atmospheric residence times and thus have little effect on regional continental background concentrations. The atmospheric oxidation of natural and anthropogenic sulfur dioxide (SO_2) is believed to be the dominant removal mechanism. Other papers are on washout (Peters, 1976), scavenging (Hales and Dana, 1979), dry deposition (Sheih et al., 1979).

Several papers on the distribution of sulfate emissions in the United States and Europe included Whitby et al. (1978), Semb (1978), Granat (1978), Yuen et al. (1979).

Effects of Acid Precipitation on Surface Water and Aquatic Ecosystems

While the long-term effects of acidic deposition on forest and other terrestrial ecosystems remain unclear, there is increasing evidence that acidic deposition is involved in the changing chemical and physical characteristics of certain lakes and streams, as well as their associated aquatic ecosystems. These changes were first observed and investigated in Sweden and Norway, followed by more limited studies in Canada and the United States. Already a very substantial body of literature exists describing these phenomena.

It has been fairly well established that there have been significant changes in a number of freshwater lakes and streams in southern Norway, Sweden, and eastern North America. The observed changes in these water bodies are essentially (a) a pH decline accompanied by disappearence of bicarbonate ions and increases in sulfate and aluminum levels, (b) a reduction in species number of phytoplankton and invertebrates, (c) accumulation of certain algal species; (d) inhibition of organic matter decomposition, and (e) gradual reductions in fish populations, especially in the most acid-sensitive species. The majority of these water bodies are distant from urban centers, industrial plants, and agricultural activities, minimizing the possibility that localized effects are of major importance. The affected lakes and streams have certain common characteristics: (a) they are underlain by granite and other highly resistant rock types poor in calcium and magnesium-containing minerals, (b) the watershed soils are thin and poorly buffered, (c) the watershed to surface area ratio is low, and (d) acidic deposition inputs are relatively large. All of these factors point toward acidic wet and dry deposition as a major contributor to the observed changes, despite uncertainties about many of the details of the acidification mechanism and the rate at which such changes have been occurring.

Most of the studies have been qualitative field surveys and laboratory experiments on the physiological responses of the biota to increased acidity. However, quantitative data to support the evident change by low pH on natural systems are now appearing in the literature. Many of the authors have reported that aquatic organisms at all trophic levels are affected by increased hydrogen stress. Acid precipitation can have adverse effects on stream and lake populations of zooplankton, phytoplankton, bacteria, invertebrates, salamanders, and fish (Lynch and Corbett, 1980).

A combination of factors in northeast North America and northwest Europe make the water systems particularly susceptible to acidification. The bedrock consists of slowly weathering granites, schists, and porphyries which render inland waters that are low in salts and are poorly buffered. Acidic precipitation at pH 4-4.5 and dry deposition therefore greatly affect the lakes. Dry deposition accounts for the high sulfur concentrations. Aluminum concentrations increase with decreasing pH from about 10 μg/L to 600 μg/L from summer to autumn yearly, and are increasing on the annual average. Above pH 5.5, aluminum precipitates due to low solubility. Organic matter increases the solubility by complexation/chelation which further aggravates the Al toxicity to organisms, especially fish. However, Al is also an efficient precipitater of humic substances and results in increased lake transparency with increased Al levels at low pH (Dickson, 1978).

* There are anti-acidity systems that tend to counter the acidification processes in natural water bodies. The sediments are a source of buffering action. Calcium is the ion of greatest adsorbed concentration in the sediments. Sulfate, being the major source of acidity originating from sulfuric acid, is reduced and this is an important process in the neutralization of the acid complex. Sulfate reduction is a strictly anaerobic process, and generally only occurs in the sediments and leads to a corresponding decrease in the strong acid concentration. Under

aerobic conditions, sulfate adsorption to the sediment surface is possible, likewise reducing acidity. Production of ammonia during organic matter decomposition also results in acid neutralization through formation of ammonium ions. Subsequent nitrification of the ammonium would have the opposite affect. At low pH of 4, streamwater concentrations of Al, Ca, Mg, K, Mn, and Fe increased, with little increase in DOC, Na, NO_3, NH_4, and other trace elements (Hall and Likens, 1980).

Seip (1980) gave an interesting overview of the sources and mechanisms of acidification of freshwater. A catchment is a very complex system and large numbers of processes play possible roles in acidification. Some important factors are CO_2 pressure in the soil, uptake and release by vegetation, weathering, cation exchange, organic acids, oxidation and reduction reactions (S and N compounds), and accumulation and depletion in the catchment. Three possible conceptual models were given. (1) a model based on a direct affect of precipitation on lakes and rivers, (2) a model emphasizing the increased deposition of mobile anions (SO_4), and (3) a model based on the affects on freshwater through a change in soil acidity caused by precipitation or vegetation changes. Based on European data, Seip concluded that the fraction reaching rivers and lakes unchanged is small, thus the direct affect of acid rain is actually small. Similarly, direct effects of soil acidification on water systems is not thought to be great. The easiest way to understand the acidification of freshwater is by considering the increased sulfate deposition. The increased concentrations of mobile anions explain at least a substantial part of the observed acidification. Therefore there seems to be no reason to doubt that the increase in the deposition of acidifying components has played an important role in the acidification of freshwater. The net loss of nitrogen and possibly phosphorus via the biota during high acidity episodes could be a significant loss from natural stream and lake systems (Hall and Likens, 1980, Meyer, 1980).

The chemistry of acid rain *per se* and its affects on impacted cenopy, soil, and water systems have been given in several excellent papers and symposia reports. Individual papers on predation include Nilssen (1980a, 1980b), DeCosta and Jenicke (1977), on decomposition of organic matter by Traaen (1980), Anderson et al. (1978), Traaen (1976, 1977), Raddum et al. (1980), papers on macrophytes by Hultberg and Trahn (1978), Grahn (1977), Muller (1980), and on phytoplankton by Giddings and Galloway (1976)

Effects of Acid Precipitation on Soil Microorganisms and Microbial Processes

A critical function of nature's nutrient cycle in the forest and field is the movement of nutrients via the various pathways in the soil Organic matter decomposition is one of the major nutrient transformation systems. Significant amounts of nutrients are transferred to the soil as litterfall, throughfall, stemflow, and directly as rainfall. This aqueous route follows a simple sequence to the soil leachate and groundwater, although the chemistry is complicated and not well researched at the ecosystem level (Feller, 1977).

Certain microbially mediated transformations in soil are essential for plant growth, food production, and environmental quality Bacteria and fungi are responsible for the decomposition of probably all naturally occurring organic compounds and many synthetic chemicals and their transformation to inorganic products. By mineralizing the organic forms of nitrogen, sulfur, and phosphorus in soil and plant remains, the soil microflora convert these elements to the inorganic state so that they are available to higher plants which do not use the complex organic materials present in soil and plant remains. Soil microorganisms also make N_2 available to higher plants through biological nitrogen fixation. They are the soil means to produce the nitrate which is readily used by higher plants and they bring about oxidation and reduction of inorganic sulfur, thereby changing the availability, toxicity, and mobility of the element.

According to Labeda and Alexander (1978), consideration of the ecological effects of atmospheric pollution on biota in the past has largely dealt with the effects on the macrobiota of natural and agricultural ecosystems, and only recently has there been any great interest in the relationship between microorganisms and air pollutants. The role of microorganisms in the production of air pollutants, such as nitrogen oxides through denitrification (Nelson and Bremner, 1970) and volatile sulfur compounds (Kadata and Ishida, 1972), has been the subject of some attention. Other studies have dealt with the microbial metabolism of the adsorbed atmospheric pollutants (Ghiorse and Alexander, 1976) and with the effects of the pollutants on algae and microbial pathogens of plants (Hallgren and Huss, 1975; Saunders, 1966, Weinstein et al., 1975).

Information on the effects of acid precipitation on microorganisms has increased in the various scientific journals since about 1976

Changes occur at the decomposer level and involve shifts from bacterial to fungal decomposition. Of the many facets of the acidification problem that need investigation, the processes and rates of change are very important. Our understanding is mostly descriptive (Schofield, 1975).

An excellent review paper on the effects of acid rain on microorganisms and microbial processes in soil was given by Alexander (1980). He concluded that nitrification ceases at pH 4-5 and below due to autotrophic bacteria, actinomycetes also decrease in number at low pHs, decomposition of humus ceases, and legume nodulation in the N-fixation process is very sensitive to low pH. This also holds true for the nonsymbiotic N-fixers below pH 5.0. Denitrifying bacteria are also sensitive to low pH.

Research on the effects of acid precipitation on microbial processes specific to Florida is given by Volk et al. (1982) and for California by Killham et al. (1983).

Effects of Acid Precipitation on the Forest Canopy: An Important Factor in the Acidification of Forest Soils

A critical function of nature's nutrient cycle in the forest is the movement of nutrients from the trees to the forest soil. Litterfall is a well-known phenomenon to almost everyone and is one of the major nutrient sinks. However, a significant amount of nutrients is also transferred along a more direct and constant route via the precipitation mainly as rainfall. This aqueous route follows a simple sequence from precipitation to canopy throughfall and stemflow to forest floor leachate to mineral soil leachate to groundwater to streamwater (Feller, 1977). However, the chemistry is complicated and is still not well understood at the ecosystem level.

Most plants can take up nutrients from the atmosphere (Tamm and Cowling, 1975). This capability is important in forests because nutrients are generally scarce. Trees develop very large canopies of leaves and branches extending high above the ground surface. Thus trees offer a very large surface for deposition, assimilation, and loss of nutrients and various substances due to the action of rainfall.

Any study of the affects of acid rain on forest soils must consider the differences in quality and quantity between rainfall and the actual input to the soil, the litter leachate (Lee and Weber, 1980). The affects of acid rain on forests indeed can only be adequately studied in an ecosystem context. Specifically, the following must be considered: (1) changes in rain chemistry caused by the passage through canopy and litter layer, (2) affects of soil solution chemistry on uptake of chemicals by plants, (3) affects on other biological soil processes, (4) effects on weathering of minerals, and (5) role of sulfate and nitrate adsorption on the various pathways to the soil solution (Lee and Weber, 1980).

Research data are now entering the various scientific journals on all the various affects. Leaching of substances from the canopy is of greatest interest to the soil scientist from the viewpoint of a constant supply of inorganic and organic ions entering the soil from the forest above.

The terms incident rain, acid rain, or rain refer to the normal rain before contacting vegetation or other substances. This could be snow, mist, fog, etc., as well as rain. Throughfall refers to the precipitation which drips down through the forest canopy. Stemflow refers to the precipitation which reaches the ground by running down the boles of the trees. The chemistry of the throughfall and stemflow includes nutrients leached from the vegetation, nutrients washed from the surface of the vegetation, and also the nutrients initially in the rainfall. The term net removal refers only to the nutrients leached from the vegetation plus that washed off the surfaces. The total annual precipitation received by a region does not all become available to the forest floor. A significant portion becomes lost from potential water sources through interception and replenishment of the soil moisture deficit (Schomaker, 1976). The term interception refers to that part of the gross incoming rain that wets and adheres to all above ground objects exposed to the weather and that will eventually evaporate back into the atmosphere. Water loss of this type is especially noticeable under dense, closed forest stands where as much as 25% of the total annual precipitation may be intercepted. The extent of interception is affected by tree species, size, tree form, storm size and intensity. It takes about 3 mm to wet the canopy before throughfall takes place (Eaton et al., 1973, Gaspar and Untaru, 1973). Interception affects throughfall chemistry by (1) retaining some nutrients in the canopy during rainfall, (2) leaching leaf nutrients but retaining a portion as evaporation salts after the storm, (3) direct absorption of nutrients into the leaves from the water on the leaf surface or by microflora, etc., on the leaves and branches. However, despite these three routes of nutrient retention, there is almost always a net increase in the concentration of nutrients in the throughfall. Miller and Williams (1973) found that the large amounts of nutrients removed from the trees by rainfall more than compensated for the losses by interception. Throughfall was found to increase with distance from the stem in *A. auriculaeformis* (Kasen, 1968). Kasen (1968) also found that interception was higher for species with rough bark and hairy leaves.

The literature review revealed percentage figures for throughfall, stemflow, and interception in six, twelve, and nine papers, respectively (Abagiu, 1973, Aldridge, 1973, Brattsev, 1973; Fellizar, 1976; Foster, 1974; Galenko, 1973; Jackson and Aldridge, 1973, Miller and Williams, 1975; Nipon, 1980, Reiners, 1972, Serafimov and Naev, 1978, Smith, 1974; Valcicak and Mendel, 1973, Weihe, 1973, Willis et al., 1975). The data represent research in 10 different countries with various data from the United States. The throughfall averaged 75%, interception averaged 20%, and stemflow averaged 1.3%, mostly in conifers. Several interesting conclusions were drawn by the various authors. For example, Weihe (1973) concluded that high interception is thought to be one cause of poor growth of spruce on sites where precipitation is low and the terrain level.

Perhaps the best conclusion has been articulated in a memorandum from the National Atmospheric Deposition Program to all cooperators, boards, and committee members (which includes one faculty member of the Department of Soil Science at the University of Florida). It was dated November 19, 1980, and concludes

Extensive research is needed to further elucidate the precise magnitude and consequences of acidification on both aquatic and terrestrial ecosystems. Long-term field studies should be initiated to determine the ecosystems' responses to different levels of acid precipitation.

Effect of Acid Precipitation on Mobility of the Major Soil Ions

Quantitative data generated from field studies on an ecosystem scale which relate ion concentrations to magnitudes of ion loss and movement to the water table and to lake systems are rare in the literature. The Hubbard Brook study in New Hampshire, the most extensive long-term field study in the United States, still remains a monitoring study of input-output via stream runoff (Likens et al., 1977).

Papers related specifically to the movement of ions through the soil are only recently numerous in the literature. Quantifying mass balances and adsorption on a large field scale has been an elusive goal. The sheer analytical effort required is one detriment. Perhaps with the expanded use of plasma instrumentation, a new impetus will result for investigating such balances.

Many review documents have been published since 1979. The Environmental Protection Agency (EPA) has been instrumental in leading a concerted attack on acid rain research nationally. Many descriptive and summary documents have also been published by such groups as Long Range Transport of Atmospheric Pollutants (LRTAP). Little research has been carried out on sensitive soils similar to the sands of Florida, which are recognized as being unique to the nation (McFee, 1980).

The literature on cation-anion exchange has been well documented *per se*. However, research into ion mobility under acid rain conditions has again only recently been initiated and the details are only now making an appearance in the scientific literature. The physics of water movement has been well documented. However, again, many of the experiments have been in the laboratory and their applicability to large scale field conditions to depth in the soil are questionable. Three-dimensional field experiments relating ion mobility to losses in the water table and lake systems are nonexistent in the literature. However, there are many recent papers that give specific information that is useful in assessing the effects of acid rain on soils.

Ion Mobilities

Electrostatically charged colloids in soils give rise to ion exchange reactions and thus provide a chemical buffer against detrimental effects of acid rain deposition. In soils which contain pH-dependent charge, colloids such as iron and aluminum oxides and organic matter, infiltration of acid rain actually decreases the effective capacity of the soil to retain cations and thus results in leaching loss of basic cations such as Ca present on the colloids. At the same time, acid rain increases the capacity of the soil to retain anions such as SO_4 (Wolk and Mansell, 1983).

Acid deposition accelerates rates of mineral weathering from watersheds. Three principal factors mediate this process: (1) soil volume and porosity, (2) soil mineralogy, and (3) runoff rate. Hydrogen ions are exchanged for cations, particularly Ca, Mg, and Al. As a result, Al concentrations may reach levels (>0.2 mg/L) known to be toxic to aquatic organisms. To date, there has been no documentation of decreased soil pH as a consequence of acid deposition although groundwater acidification is reported in Sweden (Evans et al., 1981). Based upon available data, however, it appears that differences in nutrient leaching responses in forest soils are related primarily to physical-chemical differences between soils (base saturation, sulfate retention capacity, organic matter distribution, and labile aluminum abundance), and secondarily to differences in H^+ ion loading (Cronan, 1982).

Mollitor and Raynal (1982) found that sulfate, calcium, magnesium, and sodium concentrations were significantly greater in B horizon leachates than in bulk precipitation. It also appears that organic acids leaching from the forest floors contribute a substantial concentration of organic anions. Likens et al. (1977) reported net losses of sulfate, calcium, magnesium, and sodium from undisturbed Hubbard Brook watersheds. Martin (1979) reported a net loss of calcium, magnesium, and sodium from a virgin forest in the White Mountains, but a net gain in sulfate although streamwater concentrations were slightly higher than precipitation concentrations. Cronan et al. (1978) reported higher sulfate, calcium, magnesium, and sodium concentrations in spring water than in bulk precipitation.

The bulk of the sodium and much of the calcium and magnesium lost in leachates is likely derived from and may likely be replaced by mineral weathering. Because potassium appears tightly cycled by vegetation, any acceleration in leaching of this nutrient by acid rain may be deleterious. Increases in sulfate concentration as water moves through forests are not easily explained. The dynamics of sulfur transformations and pooling are complex and not well understood. More work on sulfate, examining both organic and inorganic components of the sulfur cycle, is required (Mollitor and Raynal, 1982).

Low concentrations of exchangeable cations suggest that chronic leaching losses of nutrient cations may adversely affect forest productivity. Cation exchange capacities of acid forest soils are associated with humus and this exchange capacity is pH-dependent (Kalisz and Stone, 1980). Potential effects of changes in CEC associated with acid precipitation-induced soil pH changes deserve further investigation.

Patterns of nutrient cycling and loss are complex and differ for each situation studied. Precipitation inputs, forest type (Martin, 1979), stand age (Leak and Martin, 1975), soil characteristics, parent material mineralogy, and other factors influence nutrient dynamics (Mollitor and Raynal, 1982).

Changes in soil-pH are most pronounced at the soil surface. With increasing time of exposure or severity of acidific input, effects occur progressively deeper in the soil profile. Decreases in soil pH enhance movement of toxic elements (such as Al and Mn). The Al^{3+} is potentially harmful to plants, aquatic life, and soil microbial activity (McColl, 1981), any increases in Al^{3+} must be considered to be potentially deleterious. Soils that are silicic (e.g., granitics) with low cation-exchange-capacity, with low base saturation, and of shallow depth are most sensitive to increased acidification. Many granitic soils of the Sierra Nevada are quite sensitive, because of their immaturity, geologic parent material, and geographic location (McColl, 1981).

Hydrogen

There are two general areas of concern relative to the interactions of acidic rain with soils: (1) effects of acidic rain on nutrient leaching, soil acidification, and the nutrient status of terrestrial ecosystems, and (2) the impact of interactions between acidic rain and soils on the composition of waters reaching aquatic ecosystems. To some extent these concerns are mutually exclusive; i.e., if incoming H displaces and leaches nutrient cations from basic soils, acidification of aquatic ecosystems is prevented. On the other hand, incoming H may have little effect on the nutrient content of very acidic soils, but in sufficient amounts, H could mobilize Al which produces toxic effects in aquatic ecosystems (Cronan and Schofield, 1979).

Cation removal by internal H production and leaching (by carbonic and organic acids) exceeded atmospheric H input by a factor of 2 in the acid rain-impacted Thompson, Solling, and Jadraas sites. Cation removal by either bole or whole-tree harvesting reduces the significance of atmospheric H inputs even further, but atmospheric inputs could be considered negligible only at the unimpacted Findley Lake and H.J. Andrews sites (Evans et al., 1981).

Unfortunately, internal H production varies considerably among various forest ecosystems, and generalizations about internal vs atmospheric H inputs are hazardous. Furthermore, much of the above discussion is predicated on the assumption that H inputs to soil via either acidic rain or natural mechanisms will result in an equivalent amount of base cation removal. Since anions must balance cations in any solution, this further implies that added anions and H are mobile in soils. This assumption, while useful in conceptually exploring various scenarios, has been shown to be invalid in many instances, particularly with respect to sulfate (Johnson et al., 1979, Singh et al., 1980, Khanna and Beese, 1978).

Most soil leaching studies are developed on the premise that the soil solid phase component is "fixed" and negatively charged, and that the extent of leaching is directly related to the influx of H ions from acid rain. The buffering capacity, in turn, is related to the relative adsorption energy of the H ions in comparison with that of the exchangeable cations. As a result, the major soil variables controlling leaching are considered to be cation exchange capacity, percent base saturation, surface area, and soil pH, as well as texture, clay mineralogy, and free carbonate content. In short, the vulnerability of a soil to acidification and base depletion is inversely related to its H ion-consumption capacity. The "leaching potential" of acid rain is best described by its pH. As the pH of acid rain decreases, the potential for soil leaching increases (McColl and Firestone, 1982).

Aluminum

The studies of aluminum (Al) leaching illustrate that acid forest soils may differ dramatically in their patterns of Al transport. Despite marked differences between the sandy, excessively drained soils and the fine-textured soils, both soils showed a similar eluviation of Al from O and A horizons and accumulation in the B horizon. Thus, it is unlikely that surface waters near such soils would suffer from toxic Al transport associated with acidic deposition. In contrast, another soil showed a large enrichment of B horizon percolate with toxic monomeric inorganic Al. Transport of this aluminum-rich water to nearby streams and lakes could be potentially lethal to aquatic organisms (Cronan, 1982).

Watershed acidification greatly increases Al leaching (Gjessing et al., 1976; Cronan and Schofield, 1979) and several studies taken together support the notion that increased Al in soil pore water may reduce total P loading (Hendry et al., 1980). While less P may be removed at fixed Al concentrations below pH 5 than at pH 5 to 6, an elevated concentration of Al may result in an increase in P removal below pH 5, by whatever means, not only in the lake water but in the watershed soil as well. This topic needs further investigation (Evans et al., 1981, Budd et al., 1981).

The leaching of Al^{+3} from soils is of considerable concern as this ion is potentially harmful to fish if it reaches the aquatic system, and could limit root growth of vegetation if the concentration of the soil solution is raised sufficiently.

Leachate Al was significantly correlated ($r^2 = 0.51$, $p < 0.001$) with dissolved organic carbon (DOC). Speciation of Al revealed greater than 99% of the Al was complexed with organics which had pH-dependent behavior similar to organic acids with pH's of approximately 5.5

Complexation rather than mineral dissolution or ion exchange mechanisms appeared to control Al^{3+} levels. A direct H^+ interaction with the large pool of Al in the litter and mineral horizons could not account for observed Al levels in the leachates. Compared to simulated rain at pH 5.6, neither acid treatment (pH 4.0 nor 3.0) resulted in a change in leachate strong acidity. However, compared to 5.6 and 4.0, the pH 3.0 treatment resulted in decreased DOC and Al in the leachates. Precipitation acidity can indirectly influence Al mobility in forest soils through its interaction with the large pool of organic carbon in the litter and organic horizons (McColl and Firestone, 1982). This may explain higher Al concentrations in conifer site leachates, which are more acid and higher in organic anion concentration. This high Al mobility may have deleterious effects on aquatic ecosystems (Cronan and Schofield, 1979) and may hinder root development (Voigt, 1980).

The biochemistry of Al in soils and aquatic systems is given by Turner et al. (1983). Review papers on Al exchange equilibria are by Nye et al. (1961), Coulter (1969), and Nordstrom (1982).

Sulfate, Nitrogen, and Anion Adsorption

Sulfate is known to adsorb to Fe and Al oxides in soils where it can create exchange sites capable of retaining incoming H^+ or other cations (Johnson et al., 1979, Johnson et al., 1980, Singh et al., 1980, Khanna and Beese, 1976). Thus sulfate-adsorbing soils can be acidified by H_2SO_4 without an equivalent amount of cation leaching. Conversely, non-sulfate adsorbing soils can be leached by H_2SO_4 without an equivalent amount of acidification due to H-induced acceleration in the rate of cation weathering from soil minerals (Evans et al , 1981).

Nutritional consequences of excess SO_4 inputs are unclear. Perhaps uptake of excess SO_4 aids in charge balance problems in ammonium-utilizing forest ecosystems where uptake of cationic nutrients exceeds uptake of anionic nutrients (necessitating either HCO_3^- uptake or H^+ release from roots). Thus, while atmospheric inputs of S sufficient for average crop requirements (19 S kg S/ha, Terman, 1978) exceed forest requirements, this is not likely to cause nutritional harm to forest ecosystems. Inputs of N in polluted rain, while they do not fulfill forest N requirements, do appear to make a significant positive contribution.

Detrimental effects can occur if atmospheric H inputs significantly add to or exceed H production by mechanisms internal to the forest soil. Estimates of internal H production in forests are very rare, but the available literature gives values ranging from approximately 200 to 23,000 eq/ha/yr. Taking the low figure as an arbitrary maximum allowable H deposition rate and assuming an equivalent input of 67% SO_4 and 33% NO_3 as counter-ions provide = 3 kg S and 1 kg N/ha/yr. This amount of S input is unlikely to fulfill agricultural needs but will probably meet forest requirements in S deficient areas. Nitrogen inputs of this magnitude are probably insignificant relative to crop needs, but may supply as much as 40% of forest needs.

Nitrate can generally be considered to be totally mobile in soils, whereas sulfate mobility is largely dependent on the adsorption capacity of the soil. If high nitrate levels exist, movement of nitrate in soil to drainage water is then largely determined by the amount taken up by vegetation. Soil nutrient cations would accompany nitrate ions that are transported beyond the rooting zone.

It is obvious from Huete's results (1982) that the anion composition of acid rain has a significant role in leaching of soils with amphoteric-charge properties. Only in those soils dominated by negative-charge constitutents will anion composition have negligible effects on soil leaching. However, in oxidic, allophanic, and acid soils with sesquioxide coatings of Fe or Al, there is sufficient variable charge to potentially restrict soil leaching through anion adsorption. In such soils, the anion composition of rain will modify soil leaching to an extent determined by two interrelated factors: the anion adsorption capacity of the soil profile, and secondly, the nitrate to sulfate ratio of the acid rain (McColl and Firestone, 1982).

More recently, however, the approach in soil leaching studies has shifted from H$^+$ ion-leaching models toward anion behavior models (McColl and Cole, 1968, Johnson et al., 1979). This is based on the concept that soil leaching is controlled by the availability (and thus mobility) of anions present in the percolating soil solution where electrochemical neutrality is required. If input anions are adsorbed, soil leaching is restricted unless another anion is displaced in the process. Anion adsorption has been reported in soils ranging from highly weathered, oxidic soils to less-weathered, temperate region soils containing thin sesquioxide coatings of amorphous iron and aluminum oxides. In these soils leaching is regulated by anion flux behavior and H$^+$-cation leaching models are rendered useless. Furthermore, the buffering capacity becomes increasingly dependent on the anion adsorption properties or charge characteristics of the soil.

The presence of variable-charge constituents in a soil further complicates the study of leaching, not only due to the presence of both positive and negative charge sites, but because the solid phase has dynamic charge characteristics that are pH-sensitive. Acid rain can therefore modify soil charge properties by altering soil pH in amphoteric soils. In turn, the charge behavior in soils will control the mobility of acid rain anions and the leaching of soil cations. Specific adsorption of sulfate anions has been reported in several forest soils subjected to acid rain (Johnson et al., 1979, Johnson and Henderson, 1979). The restricted mobility of sulfate was found to regulate soil leaching fairly well. Unlike sulfate, nitrate anions are not specifically adsorbed and nitrate mobility is usually unrestricted. The relative flux behavior of these two acid rain anions may therefore considerably modify soil leaching over varying nitrate-sulfate contents.

In one experiment, Huete (1982) used four acid mixtures of H_2SO_4 and HNO_3 at pH 3.5 with varying sulfate to nitrate ratios (100:0, 60:40, 40:60, and 0:100%, respectively) to leach three soils: an Ultisol from a mixed-conifer forest in California, an Oxisol from a semi-deciduous forest in Brazil, and an Entisol from an annual grassland in California. These three soils had very different charge properties. The Ultisol had a high anion adsorption capacity, because of its high Fe_2O_3 content (1.2%) and high point-of-zero-charge (PZC) (6.0). The Oxisol, although strongly weathered, had lower Fe_2O_3 content (0.5%) and PZC (4.5). The Entisol was a relatively unweathered alluvial soil from siliceous rock, with less Fe_2O_3 (0.3%) and a lower PZC (3.5), and thus was representative of a fixed-charge soil.

Results of leaching experiments showed that cation leaching in the Ultisol decreased in direct proportion to nitrate content, while the relative nitrate-sulfate content made no difference in cation leaching in the Entisol. Oxisol leaching was intermediate between the other two soils (McColl and Firestone, 1982).

Anion mobility in the soil is important in assessing the impact of acid precipitation on nutrient cycling and loss (Johnson et al., 1980). Since sulfate is the dominant anion in acid precipitation (Galloway et al., 1976), the mobility of sulfate and internally generated organic anions probably influence, at least to some extent, the degree of cation leaching. Sulfate mobility appears related to soil iron and aluminum sesquioxide content (Johnson et al., 1979, Singh et al., 1980, Swoboda and Thomas, 1965). Organic anions may also be retained within the soil profile during the development of Spodosols. It is thought that organic anions translocate cations within the solum, while below the solum, bicarbonate leaching (Ugolini et al., 1977) or sulfate leaching (Cronan et al., 1978) dominates.

The present data suggest that sulfate and organic anions are mobile in these soils. Sulfate and organic anion leaching are of roughly equal importance in the hardwood site, and organic anion leaching dominates in the conifer site. An additive affect of sulfate and organic anion leaching may account for the higher cation concentrations and lower pH of conifer B horizon leachates. Also, as organic matter may block retention of sulfate in soils (Johnson et al., 1980), the abundance of organic anions in conifer site solutions may help explain greater sulfate concentrations in water leaving the conifer site solum. Because carbonic acid does not dissociate significantly below pH 5.0 (Galloway et al., 1976), bicarbonate concentrations are likely very low in these soil leachates.

Papers related to acid precipitation in Florida were Woltz and Howe (1979), Hendry and Brezonik (1980), Hendry et al. (1980), Bitton et al. (1983), Canfield (1983), Brezonik et al. (1981), Volk et al (1982), and Volk and Byers (1983). A series of papers was in a publication by Green and Smith (1983). Other papers on sulfate and modeling were by Christophersen and Wren (1981), Reuss (1980), and Singh et al. (1980). A paper by Talsma et al. (1980) showed chloride adsorption with depth. Papers on tracers were by Dahl et al (1980) and Ahuja and Lehman (1983). Papers on N, S, and H sorption are given by Nipan (1980) and Singh (1980) and for H budget by Rosenqvist et al. (1980). A comprehensive long-term report on biogeochemistry of a forested ecosystem was by Likens et al. (1977). A summary of the effects of acid precipitation on soils, soil microorganisms, aquatic systems via soils, and mobilization of soil elements was compiled by Linson (1981).

CHAPTER 3
MATERIALS AND METHODS

Field Experiments

Irrigation Experiments

Location of site

The site of the study was a soft water lake, McCloud Lake, and its small (1 km^2) uninhabited watershed located about 15 km east of Gainesville in the Katharine Ordway Preserve, a 3000 hectare property of the University of Florida. Geographically, its location was in the Trail Ridge region of the Central Highlands in northern Florida, an area with karst topography: numerous sandhills interspersed by small lake basins resulting from solution of underlying limestone. The McCloud Lake watershed contains no surface streams, reflecting the very porous nature of the fine sandy soil. Downward seepage is rapid, and surface runoff is exceedingly low (Figure 3-1).

Vegetation in the watershed is impoverished, reflecting the weathered and infertile soil and its poor water-holding capacity. Woody vegetation consists primarily of longleaf pine and turkey oak with an open canopy. Wiregrass dominates the herbaceous layer and lichens are common on the soil surface. Pocket gopher and gopher tortoise burrows are formed, along with dirt piles thrown up by beetles that burrow as

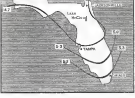


Figure 3.1. Lake McCloud acid rain experimental site.

much as 6 meters deep. However, the plot sites *per se* were relatively devoid of these characteristics.

The soils are fine marine sands, kaolinitic sands, and sandy clays of Recent and Pleistocene Age. These deposits are fairly deep, about 3 to 10 meters and are underlain by a confining layer (25 to 35 m) of phosphatic sands and clays with low permeability. Underlying this formation are deep limestone deposits that form the Florida Aquifer. The soil is a Typic Quartzipsamment. The study site was located on the south side of the lake above the grass line on a 13% slope. The average annual rainfall is 140 cm. The mean annual temperature is 21.5°C.

The lake site was chosen for the study since two concurrent and joint EPA projects were funded to research the effects of acid precipitation on lake and soil chemistry. The lake, having an area of five hectares and being about 5 meters in depth, is a soft water, low conductivity oligotrophic lake with a chemical composition similar to that of natural rain for the region. Thus the lake water served as a source of irrigation water for the soil study, having an ionic strength of 45 decisiemens per centimeter (dS/cm).

Soil description

Taxonomic classification: Hyperthermic, uncoated Typic Quartzipsamment.

Typical pedon: Candler sand, forested.

HORIZON	DEPTH	DESCRIPTION
A1	0-10 cm (0-4")	Dark grayish-brown (10 YR 4/2) fine sand, single grain, loose, many clean sand grains, many fine and medium roots, strongly acid, clear smooth boundary. 1380
A21	10-23 cm (4-9")	Brown (10 YR 5/3) fine sand, common, medium, distinct, grayish-brown (10 YR 5/2) mottles, clean sand grains, many fine and medium and few large roots, strongly acid, clear wavy boundary 1381.
A22	23-51 cm (9-20')	Light yellowish-brown (10 YR 6/4) fine sand, few, common, grayish-brown (10 YR 5/2) mottles, single grain, loose, many clean sand grains, common fine and medium roots, strongly acid, clear wavy boundary 1382.
A23	51-122 cm (20-48")	Brownish-yellow (10 YR 6/6) fine sand, single grain, loose, many clean sand grains, few fine and medium roots, strongly acid; gradual wavy boundary 1383.
A2&B	122-203 cm (48-80")	Very pale brown (10 YR 7/4) fine sand, single grain, loose, brown (7.5 YR 5/2) loamy sand lamellae about 1 to 3 mm wide and 3 to 6 mm long, many clean sand grains, few roots, strongly acid. 1384.

Drainage and permeability. Excessively drained, slow runoff, very rapid permeability. The water table is at depths greater than 200 cm.

Geographic setting. Candler soils normally occur in nearly level to strongly sloping landscapes. Slope gradients are dominantly 1 to 12 percent. The soils are formed in thick beds of eolian or marine deposits of course-textured materials (Appendix VIII).

Distribution and extent. Peninsular Florida. The series is of moderate extent.

Site description

Transect layout. An engineering plan was designed and equipment was installed to transport the irrigation water to the plot sites using the lake as the water source (Figure 3.2).

Three transects, each consisting of three plots, were placed on the south side of the lake. The transects were placed parallel to each other and approximately 30 meters apart projecting perpendicular to the lake and extending upslope. The plots within the transects were approximately 30 meters apart. The plots nearest the lake in each transect were approximately 30 meters from the lake edge and above the grass line. All plots were 75 m^2 in area. The distances between transects and plots within transects were chosen so as to minimize aerial drift among and within treatments imposed on the plots. The large plot size was chosen (1) to ensure adequate working area for the various experiments and equipment involved regarding placement and (2) for possible inclusion of additional experiments (Figure 3.3).

The three transect mainlines, the nine plot lateral lines, and the 36 within-plot sprinkler lines were polyvinyl chloride, schedule 40, to withstand 600 kiloPascals (kPa) of pressure. Flowline pipe diameters were 6.25 cm at the pump, 3.75 cm on the mainlines, 2.54 cm on the lateral lines, and 1.35 cm on the plot lines.

Mainline equipment included a float, pump, flowmeter, and two chemical liquid injectors. Mainline and lateral line controls included gate valves and pressure gauges. Impact sprinklers were placed at the termination of the plot lines, four per plot, for a total of 36.

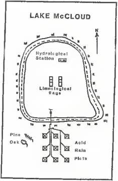


Figure 3 2. Lake McCloud and location of acid rain plots.

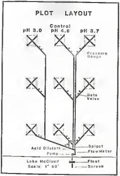


Figure 3.3. Transects and plot layout.

Mainline instrumentation

i) Float. The float consisted of a 19 L metal cylindrical drum attached to the mainline on the suction side of the pump and extending into the lake. Attachment to the mainline pipe was by the use of bicycle tubes. Placement on the mainline was such that the end strainer was elevated well above the lake bottom but far enough below the lake surface so as not to create a vortex during pumping operations.

The inlet of the mainline was a metal cylindrical strainer. A fine mesh screen was also attached around the strainer to prevent the flow of any suspended lake materials to the pump through the strainer on the suctionline. The screen was replaced several times during the experiment.

ii) Pump. The pump was a Homalite aircooled pressure pump Model FP250. The driving motor was a 10 H.P. 4-cycle gasoline engine which operated at 1500 rpm with a 3600 rpm maximum. Maximum capacity was 47,300 L/h with a total head of 92.3 m and a priming lift of 5.8 m at sea level. The maximum discharge pressure was 772 kPa. Operating capacity was 17,000 L/h and discharge pressure of 433 kPa.

iii) Flowmeter. The flowmeter was a Badger Recordall Disc Meter Model 70. Normal flow limits were 4.5 to 379 L/min with a normal operating capacity of 266 L/min. A magnetic coupling eliminated friction load and drag with an accuracy at 284 L/min of -1%. Field operation was at 284 L/min.

iv) Chemical injector. Liquid chemical injectors were used to meter the acid treatments into the mainlines for distribution to the plot sprinklers. These "chemilizers" consisted of a plastic housing with an attached inner plastic bag (which retained the acid solutions) and a control panel. The control panel consisted of a knob adjustment for bypass water control and one for acid injector volume control. Settings were made by adjusting a floating ball in both cases. A gate valve on the mainline controlled the bypass water volume with final adjustment made by the bypass knob control. (Since the bypass water also entered the housing and pressurized the acid reservoir bag externally, there was a constant pressure on the acid entering the system. This allowed for fine adjustment at the specified flow rate and assured a precise flow rate even at low reservoir volumes.) Once pressurized, the system was very stable and required only periodic fine adjustments (Figure 3.4).

A calculated flow rate of 95 L/min was used on each mainline transect (three plots) with a bypass flow rate of 11 L/min, and an acid injection flow rate of 91 mL/min. This was a 1:1000 dilution. The acid concentrations in the acid reservoirs were such as to give the designated treatment pH after 1:1000 dilution.

Controls.

i) Gate valves. A gate valve was placed on each mainline above the pump for flexibility in mainline operation of the system and for partial irrigation if required. Adjustable gate valves were also placed on all laterals in order to equalize flow rates on all plots.

ii) Pressure gauges. Pressure gauges were placed on each lateral line to monitor flow pressures and enable fine adjustment to assure equal flow rates to all plots. Pressure gauges were also placed on each mainline and one above the pump. The stepdown pressures used were

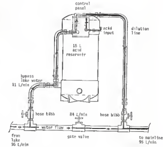


Figure 3.4 Acid injection system used in applying the treatments to the field plots

433 kPa at the pump, 366 kPa at the mainline, 300 kPa at the lateral plot lines, and 266 kPa at the sprinklers.

iii) Spigots. Spigots were placed on each of the three mainlines above the chemical injectors. These three spigots were used to sample the treatments on each transect for on-site monitoring of the acidity (pH) and EC (electrical conductivity).

Plot layout and instrumentation. The dimensions of each plot were 8.7 x 8.7 m or an area of 75 m^2. Plot instrumentation included impact sprinklers, tensiometers, manometers, respiration basins, soil solution samplers, and neutron probe tubes (Figure 3.5).

i) Impact sprinklers. Impact sprinklers were placed at each corner and adjusted to swing slightly more than 0.25 circle pattern. The sprinklers were plastic with an antibacksplash arm and a distance control baffle and delivered 8.7 L/min at 266 kPa.

ii) Tensiometers. Jet-Fill tensiometers were placed at 15, 45, and 75 cm depths, with one plot having tensiometers placed at 15, 30, 45, 60, 75, and 90 cm depths throughout the irrigation study. The tensiometers consisted of a porous ceramic cup glued to a clear plastic tube to which was connected a screw-top reservoir. The reservoir consisted of a rubber cap and a spring-loaded plunger for refilling the main tube. A side-arm suction gauge was attached and angled for easy readout.

iii) Mercury manometers. Later in the study mercury manometers were constructed and placed in the three plots of the center transect. They were carefully placed at 15, 30, 45, 60, 75, and 90 cm depths in the center of each plot, the access hole having been made using a special

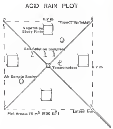


Figure 3.5 Acid rain plot instrumentation during acid rain study

bore tube. The manometers consisted of a cypress board which was driven into the soil in an upright position. Frontally attached was a small wood platform onto which was set and strapped a clear glass bottle used for the mercury reservoir. A water layer was placed on the mercury in the bottle. A calibrated metal strip was nailed to the board above the mercury bottle for readout in millimeters of mercury (Hg). Spaghetti tubing was used as a carrier for the water to each manometer tube and the tubing was stapled vertically alongside the calibrated strip. Readout of the mercury level in the tubing was made by adjusting a ruler horizontally for each visual readout. The manometer tubes consisted of a porous ceramic cup glued to a clear plastic 1.25 cm diameter tubing. The manometer tubing extended 15 cm above the soil surface. A soft black stopper was the contact between the spaghetti tubing and the manometer tube thus providing a continuous water column from the mercury to the porous cup soil interface.

The ground level "zero" was set for the calibrated strip by placing a beaker of shallow water at ground level and filling a length of spaghetti tubing to provide a continuous column of water from the ground level to the mercury reservoir. The height of the mercury rise in the column was designated the "zero" level and the calibrated scale "zero" was set at this level.

In order to create a continuous water column in the manometer, the spaghetti tubing was filled with water using a hand pump to suction the water from above the mercury in the reservoir. When lowered to near the manometer tube at ground level, a siphon system was initiated and the stopper was then inserted into the previously filled manometer tube.

This completed the water column and eliminated air bubbles in the column. This purge procedure was also followed periodically to eliminate air bubble problems. Cupric sulfate was added to the water in the column to eliminate algal growth.

iv) Soil solution tubes. The soil solution sample tube consisted of 2.54 cm diameter thick-walled polyvinyl chloride tubing. A fritted glass disc (2.54 cm D. x 0.1 cm T.) was glued to the bottom end. The contact joint was buffed smooth after drying. A black rubber #5 stopper was fitted with a 0.66 cm D. x 5 cm L. glass rod, and inserted tightly into the open end of the PVC tubing. A 7.5 cm L black latex tubing was fitted onto the glass tubing protruding above the stopper to which was attached a pressure screw clamp.

The sample tubes were placed very carefully into the bore holes which had been accessed using sharpened PVC piping of the same diameter and calibrated in centimeters for placement at the proper depth. Care was taken to ensure complete contact of the soil:disc interface. All sample tubes were placed randomly but were evenly distributed among the four quadrants of each plot. The tubes were individually numbered chronologically across plots.

The depths of tube placement in 1961 were 15, 45, and 75 cm in two treatment transects (six plots) in quadruplicate replication for a total of 72 tubes. In addition, sample tubes were placed in duplicate at 30 and 60 cm depths for a total of 84 sample tubes. For 1982 irrigation experiment, sample tubes were placed at 15 and 75 cm depths in three transects (nine plots) with each depth being replicated six times for a total of 108 sample tubes.

Suction was drawn prior to irrigation by loosening the clamp, inserting the probe of a hand suction pump snugly into the latex tubing, and drawing 500 cm suction, reclamping, and removing the end of the hand suction pump.

Sampling postirrigation was accomplished by unscrewing the clamp to release the suction and allowing easy access to the main tube. The sampling device consisted of a trigger-type hand suction pump which was attached to a 60 mL plastic sample bottle by latex tubing connected to a glass tube inserted into a rubber stopper. Also attached to the rubber stopper was a spaghetti sample probe which was inserted to the bottom of the soil solution sample tube. Thus the whole device could be manipulated with only two hands as the sample was being taken and the suction maintained by the hand pump.

The soil solution sample tubes were checked in the laboratory for air leaks prior to installation in the field plots. In order to minimize deterioration due to exposure to the weather, the rubber stoppers were coated with silicone and the clamps were lubricated with fish reel grease. After the first year's irrigations, the soil solution sample tubes were returned to the laboratory, dried, rebuffed, and retested for air leaks and clogging from clay particles. Some tubes were necessarily discarded and replaced.

Postirrigation sampling volumes were recorded so that a record of performance was maintained in each sample tube. Those sample tubes which consistently drew small volumes of soil solution or colored sample solutions were discarded and replaced by a new sample solution tube placed in a different plot location.

v) Neutron moisture tubes and probe. Aluminum tubing 5 cm D. was placed to a depth of 120 cm in the center of each plot. In addition, tubing was placed at 320 cm depth in two plots located in the center transect in the lower and upper plots. These tubes were used as access channels for the neutron moisture probe. Since the soil is a medium sand even at great depths, a stone base was first raised in the bottom of the access hole before inserting the aluminum tubing. The aluminum tubing extended 10 cm above the surface of the soil in order to provide the correct contact for the clamp jaws of the neutron probe. When not in use, an inverted bottle was used to cover the tube to prevent access by rain (natural and irrigated) and animals or plant debris. Readings were taken intermittently pre- and postirrigation on many irrigations to establish the normal soil-water characteristics. In addition, hourly reading pre-, during, and postirrigations were taken saveral times to establish flux patterns in this sandy soil.

The instrument used was a Troxler Model 1651 Depth Moisture Gauge. It consisted of a Moisture Probe, a fitted cable, a Shield, and a Standard. The probe was a Boron Trifluoride tube mounted at one end and at the other end was a preamplifier with a cable connector. The Shield and Standard provided automatic radiological safety during transportation and storage of the moisture probe, and an efficient means to introduce the probe into the access tubing. The output of the Gauge was evaluated with a scaler. The probe used contained 100 millicuries of Americium-Beryllium sources with a surface radiation of 1 millirem per hour or less.

Operating parameters

Total dynamic head. Total dynamic head calculations were made by calculating and summing pressure head, 3 mainline friction heads, lateral line friction head, 3-parts per transect, elevation head, and suction head or lift. The total dynamic head for the three transects was 47.6 m.

Pump efficiency. The pump efficiency of the FP250 was calculated to be 57%. At a total dynamic head of 49.8 m the pump will deliver 530 L/hr. Our operation demands 284 L/hr. Thus the pump was operating at about 54% capacity or about half throttle.

Adding H_2SO_4 and NO_3 to the system.

i) Treatments. The treatments were control (at a pH of 4.6), pH 3.7, and pH 3.0. These acidities correspond to 19.95, 199.5, and 1000 μeq H/L. The two treatments pH 3.7 and pH 3.0 when using the lake water will have to be supplemented with 179.6 and 980.1 μeq H/L.

ii) Stock solution concentrations. Sulfuric and nitric acids at a ratio of 7:3 (v/v) were used to simulate the acid rain at the lake site. A mixture of these two acids at this ratio renders a 30.0 Normal solution. This stock was prepared in the laboratory for field use.

iii) Intermediate stock solution. Since calculations were made indicating that the final dilutions were to be 1:1000 at the injector level, the intermediate stock solutions for the two treatments (pH 3.7 and pH 3.0) were dilutions of the concentrated stock at ratios of 1:167 and 1:30, respectively. These intermediate solutions were prepared in the field by diluting 91 ml and 494 ml, respectively, of stock solution to the four gallon level in plastic carboys and mixing well. These intermediate stock solutions were then transferred to the reservoirs of the chemical liquid injectors. At 3.3 gpm (95 ml/min) the total quantity of intermediate stock solutions used for a 2.5 cm rain was 5.7 L and for a 5 cm rain was 11.4 L.

iv) pH of the acid rain using the chemilizers. By calculation, the pH of the final dilutions (i.e., the acid rain imposed on the plots using the 30 N acid concentrate mixture and the ratio dilutions of 167,000 and 30,000) would be 3.7 and 3.0, respectively. The average Hs (expressed as pH) reaching the plot surfaces for all irrigations were 3.75 and 3.06, respectively. The pH of the control was 4.63

v) Sulfate and nitrate in the acid rain. By calculation, the sulfates of the final dilutions for the 3.7 and 3.0 treatments were 46.8 and 14.5 mg/L, respectively. The average sulfate concentrations for all irrigations both by calculation and determination for the 3.7 and 3.0 treatments were actually 41.6 and 13.7 mg/L, respectively. The sulfate for the control was 7.3 mg/L. Similar calculations for the nitrate for the two treatments were 10.3 and 2.4 mg/L, respectively. The actual concentrations were 8.9 and 2.2 mg/L, respectively (i.e., 2.33 and 0.49 mg/L NO_3-N, respectively).

Irrigation control on the chemical injectors. The flow rate of 95 L/min when injected with 95 ml/min of acid solution resulted in a 1:1000 dilution of the injected acid solution. The right-hand knob on the control panel regulated the acid injection solution. An input of 95 ml/min was approximately midscale. The actual dilution at the injection point in the bypass control line was 1:125 when the bypass flow rate was 11.4 L/min. A further dilution of 1.8 occurred as the bypass line reentered the mainline. Total mixing did not take place until the waterfront neared the lateral lines since there was mixing time required as the water flowed along the mainline to the plots. This was a good reason to have adequate distance between the pump:metering instrumentation and the plot sprinklers.

Irrigation time. A 2.5 cm rainfall on the three plots of a transect represented 5689 L. At a flowrate of 95 L/min, the time required for irrigation was 1.00 hours. For a 5 cm rainfall, the time required for irrigation was 2.00 hours. Since all three transects could be irrigated by the pump simultaneously, a 5 cm rainfall could be imposed on the three transects for three treatments in 2.00 hours.

Quantity of water applied. The total quantity of water applied to all transects during a 2.5 cm rainfall was 17,067 L. During 1981, the 50 cm acid rain imposed during the irrigation period totalled 341,340 L. During 1982, a total of 682,700 L was imposed. Thus the total water applied for 1981 and 1982 was 1.02×10^6 L.

Irrigation patterns. The plot sprinklers arc in a pattern of 0.25 circle and were set to swing to the plot boundary. Sprinklers so placed at each corner of a square to deliver water in an arc, the boundary of which did not reach the opposite corner. Thus there was a portion of the square plot in each corner which was irrigated by only three of the four sprinklers. This area represented approximately 15% of the plot or about 4% of the plot surface per corner. Thus there was an octagon-shaped area in the plot which was irrigated by all four sprinklers. Soil solution sample tubes could not be placed near the sprinklers.

Coefficient of uniformity. Coefficient of uniformity (CU) determinations for rainfall distribution patterns were carried out on all plots by placing basins in concentric circles from the center to the extremities of the plots, 15 basins per plot. Volumes of collection water were measured in each basin after a one hour irrigation. Coefficients of uniformity were determined for each plot. In some instances sprinklers were adjusted to give a CU of at least 85% which indicated that the irrigation spray pattern was uniform across the plot during a period of calm winds. If there was a wind of 15 km/hr or greater, irrigation was delayed.

Flow meter. The flow meter, measuring flow of irrigation water in gallons, was used to estimate closely the rate of flow by using a stopwatch. The flow rates in ℓ/min were calculated by dividing the volume of flow in gallons for a specific time period by the time in minutes and multiplying by 3.785.

Neutron probe and volumetric water content. The scaler attached to the neutron probe measured the H volumetrically by a counter with digital display. Previous calibration established a conversion equation which nullified background and expressed the volumetric water content as a percentage. The equation was

$$\text{Volumetric Moisture (\%)} = \frac{\text{Probe reading} \times 24.6445}{\bar{x}\ \text{background (shield)}} - 1.62$$

Irrigating

Stepwise procedure for irrigating

1) Prepare acid in laboratory

ON SITE

1) Dilute acid into carboys, mix well, and fill chemilizers

2) Place irrigation catch basins in plot centers

3) Open all gate valves if not adjusted from previous irrigation

4) Take gallonage reading on flow meter

5) Read neutron probe in plot tubes

6) Read tensiometers and manometers

7) Pull choke. Start pump. Pull start. Close choke. Pull vacuum handle and hold until meter blows out. Close valve and release handle. Pressure will increase as flow rate increases. Throttle down to about 1/3 throttle. Let system pressurize to about "65 psi"

8) Make a quick check of the nine gate valves so line pressure is "40 psi" to all plots. Adjust if necessary

9) Shut down gate valve on mainline at Chemilizer until flow rate in bypass line through the Chemilizer is about "3 pgm." Let stabilize by watching the floating ball. Slowly turn on acid control to a flow of about "3 gpm." Let stabilize. Open gate valves on inlet and outlet to Chemilizers

10) If running both Chemilizers, repeat on second Chemilizer

11) Read flowmeter gallonage and use stopwatch for timing. Arbitrary times can be used if flow readings are taken concurrently and recorded. Repeat often during the irrigation and calculate immediately in case fine adjustment is needed at the pump. Flow rate should be 25 gpm for each transect for 2.5 cm/hr rainfall

12) Set up EC and pH meter monitoring station. Obtain samples from spigot on each mainline and read immediately for EC (and pH, if required). The EC readings for control (pH 4.6), pH 3.7 and pH 3.0 should be 44, 116, and 445 μmhos, respectively. If not close to these readings, adjust the control on the Chemilizer and repeat. Retain samples for confirmation in the laboratory. Recheck throughout irrigation

13) Check pressure gauges on all lines periodically

14) Check sprinkler performance periodically

15) When nearing end of irrigation, shut down acid control, then open gate valve full. Bypass flow should stop and all balls return to stationary "0" position. Close gate valves (inlet and outlet) at Chemilizers

16) Shut down throttle on pump but do not shut off pump

17) Take flowmeter reading

18) Release pressure valves on Chemilizer acid and bypass sides. Open reservoir drain valve and let bypass water drain. Disconnect Chemilizer lines, open acid port, and pour acid into carboy, not onto ground. Retain for next irrigation. Open one gate valve on one of the disconnect lines to get a flow of water and use this flow to thoroughly clean and rinse the acid bag and controls and the exterior of the Chemilizer. When completed, wash down platform and then shut off the pump

19) If data for soil moisture are required, take neutron probe readings

20) Collect the irrigation samples in each plot (from Step 2) and pour into small plastic bottles for lab analysis. (Note: If taking height measurements for cm of rainfall, measure depth of water in basins before collection of sample and record.)

21) Collect water table samples if required

22) Collect lake sample in plastic bottle

23) Cover Chemilizers with tarp and secure. Cover pump with tarp (after it cools) and secure. Check gasoline in gas can to ensure enough for next irrigation

24) Clean up the premises

25) Go for a swim in the lake and praise God for another successful day

Monitoring stations during irrigations.

1) Liquid chemical injector control panel

2) Chemistry of acid treatments by EC and pH meters from spigots

3) Pressure gauges on pump, mainlines, and lateral lines

4) Flowmeter above pump for flow rate using stopwatch

5) Irrigation water catch basins for chemistry and volume delivered
6) Gas level in pump
7) Sprinkler performance spot checks
8) Be aware of pump noise and any changes in pitch
9) Acid level in liquid chemical injector

1981 irrigation program. Two treatments were imposed on two transects. Each treatment consisted of three plots replicated. The treatments were control (pH 4.6) and pH 3.7, using sulfuric:nitric acids at 7:3 ratio (v/v) in the treatment irrigations. Soil solution samplers were placed at three depths, 15, 45, and 76 cm, with four tubes placed at each depth in each plot. Soil solution samplers were also placed at 30 and 60 cm depths, two tubes per depth per plot. Thus 96 soil solution samplers were placed in the six plots.

Sixteen irrigations were made during the period March to August, 1981. The soil solutions were sampled at 48 and 96 hours post irrigation. Sixteen 48-hour and eleven 96-hour postsamplings were taken for a total of 27 sampling periods.

Fifty centimeters of simulated acid rain were applied to the irrigation site for a total of 287,660 liters. Tensiometer readings were taken throughout the period. Chemical parameters determined on the soil solution leachates were pH, electrical conductivity (EC), Ca, Mg, K, Na, Al, NH_4-N, NO_3-N, SO_4, PO_4-P, Cl, Zn, for a total of 14729 determinations from 1339 samples.

Soil samples were taken pre-, during, and post-irrigation to a depth of 90 cm at 15 cm intervals. Samples were not composited over treatment within plots. Sequential extractions of the soils using neutral N NH_4OAc

were performed for exchangeable bases. Samples were also analyzed for CEC, ex. acidity, ex. bases, and percent base saturation, as well as sand fraction separation and other soil characterization parameters.

1982 irrigation program. Three treatments were imposed on three transects. Each treatment consisted of three plots replicated. The treatments were control (pH 4.8), pH 3.7, and pH 3.0, using 7.3 (v/v) sulfuric-nitric acids in the treatment irrigations. Soil solution samplers were placed at two depths being 15 and 75 cm with six tubes at each depth in each plot. Total number of soil solution samplers placed in the nine plots was 108.

Eighteen irrigations were made during the period March to August, 1982. The soil solutions were sampled at the 48 hour post-sampling period. One sampling at 96 hour post-sampling period was taken, for a total of 19 sampling periods.

One hundred centimeters of simulated acid rain were applied to the irrigation site for a total of 715,365 liters. Tensiometer and neutron probe readings were taken throughout the period. Chemical parameters determined were pH, electrical conductivity (EC), Ca, Mg, K, Na, Al, NH_4-N, NO_3-N, SO_4, PO_4-P, Cl, for a total of 10872 determinations from 1863 samples. Two chemical injectors were used. Mercury manometers were also constructed and installed in three plots of the center transect.

Soil samples were taken pre- and post-irrigation periods to a depth of 90 cm at 15 cm intervals with lesser depths taken periodically at lesser increments at the surface of the soil. Similar analysis as in 1981 was also repeated.

Flux Experiment

Plot layout

Another follow-up study was done in the fall of 1982 to gain more information on the chemistry of the soil solution at greater depths and to characterize the flux of water to the water table as to time and magnitude. One control plot was sacrificed for this experiment. Twenty-two samplers were placed in the plot, six each at the 15 and 75 cm depth and 5 each at the 160 and 300 cm depth. One treatment was imposed consisting of 3.0 pH irrigation water with potassium iodide (KI) added at 10 mg/L iodide. One irrigation was imposed totalling 37 cm simulated acid rain over a six-hour period. The manometer in the plot center was expanded to include tubes at the 160 and 300 cm depth. Six deep wells to below the water table were installed with one in the lake, three between the lake and the plot, one in plot center, and one above the plot. This well transect extended 30 meters from the lake and 30 meters beyond the plot side upslope. Eight impact sprinklers each delivering 16.3 Lpm were installed in the plot for an irrigation rate of 10 cm/hr. Six post-irrigation samplings were taken from the soil solution samplers as well as six post-irrigation samplings from the wells. Neutron probe, tensiometer, and manometric readings were taken throughout the post-irrigation period of 14 days. The water table fluctuations were continuously monitored by automatic well level recorders mounted on each well casing. Parameters determined were as during the March-August period plus iodide (Figure 3.6).

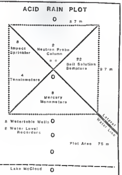


Figure 3.6 Acid rain plot instrumentation during flux experiment.

Deep wells

Since five of the six wells were on land, the well holes were dug using a 12.7 cm O.D. bucket auger. The bore holes were excavated to 30 cm below the water table. Diagonally circular perforations were cut on the bottom 60 cm of the 10 cm I.D. PVC well casing before insertion of the casing into the bore hole to below the surface of the water table and securely into the soil sand foundation. It was important to place the casings vertical to the water table since the well recorders required vertical extension of the float inside the casing to the water table surface. The bore holes were backfilled and tamped securely around the casing which extended approximately 4 m above the soil surface. One well was also placed in the lake approximately 5 m from the edge of the lake and in 0.5 m water depth. A shroud was placed around the casing to eliminate the detection of wave action by the float. This well was used to record the lake level fluctuation during the flux experiment. The 6-well transect bisected the plot with one well being placed 30 meters above the plot center for a vertical depth of 9.8 meters and a distance of 60 meters from the lake edge. This well layout using the recorders made it possible to determine the post-irrigation water table profile and to monitor the flux of the mounded water post-irrigation both vertically and in two directions horizontally (Figures 3.7, 3.8).

Platform and floats

A platform was constructed and attached to the top of the well pipe. It consisted of a 60 cm L. x 60 cm W. x 0.5 cm T. plywood base with a

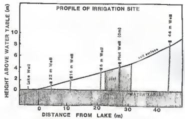


Figure 3.7. Vertical profile of irrigation site during the flux experiment.

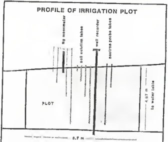


Figure 3.8. Vertical profile of acid rain plot and instrumentation during the flux experiment.

10 cm offset center hole. Another offset center hole was drilled to allow the counterbalance strap to move freely. A 10 cm PVC connector was attached to the underside of the platform using screws and angle brackets. This collar assembly was then lowered over the well pipe and fitted snugly. This allowed for easy removal of the platform. An automatic water level recorder was placed on the platform. Floats and counterweights were constructed using polyethylene bottles filled to the proper levels with a mixture of sand and water. An optimum amount of water and sand mixture was determined to permit the well float to settle and stabilize so as not to submerge nor contact the inside of the well pipe. A 4.7 ratio weight of the mixture was then placed in the counterweight bottle and sealed. The strap was attached through an eyebolt, the float was lowered into the well, the strap was placed around the recorder wheel, and the counterweight was lowered freely into position beside the well pipe and below the platform. Enough distance remained for horizontal slight windswing and above-ground vertical movement of the counterbalance for water table fluctuations. Six such assemblies were constructed and mounted. The perforated casings allowed for the free access of percolating irrigation water into the well and thus fast response by the recorder.

Automatic well level recorders

The portable liquid water level recorders (Model Belfort 5-FW-1) consisted of a chart mounted on a gear-driven drum, a pen mounted on a gear-driven arm, and an adjustable wheel mounted on the same shaft and on which the float strap was located. Several combinations of gears could be chosen, one set controlling the speed of drum rotation and one set for the ratio of arm swing length to water level rise or fall. A 5:12 ratio was chosen giving a vertical 12.5 cm chart distance for a 30 cm water table rise or fall. All chart baselines were established on the same chart gridlines and zeroed with the lake level during the experiment. The clock wind mechanism was for a period of eight days. However, the charts were changed every 24 to 48 hours since the chart speed was one rotation every 6 hours for good resolution during fluctuation period. The pen nib reservoirs were carefully monitored and levels of ink maintained above half-full at all times. A removable cover protected the recorders during irrigation.

Electric contact gauge

An electric contact gauge was used to establish the profile of the water table with distance from the lake. It consisted of a metal cylinder with a contact point to which was internally wired a calibrated plastic 50 meter measuring tape. The tape was attached to batteries imbedded in the handle of a freely rotating wheel. When the tip of the point on the cylinder contacted water, the circuit was completed and a light mechanism was activated on the handle of the reel. The water table levels were determined by lowering the measuring tape and attached cylinder into the well pipe until the light was activated as the tip contacted the water surface. A depth reading was taken from the top edge of the well casing. The distance from the ground level to the top of the well casing was then subtracted for the depth of the water table below the ground surface. A series of readings were taken in this manner on all wells throughout the irrigation experiment.

Sampling of wells from the water table

Spaghetti tubing was attached to the calibrated tape to extend 2 cm below the point of contact of the electric contact gauge. The tape assembly was lowered through the well port of the platform to the water table. At point of contact the light was activated which signalled that the spaghetti tubing was in position below the water surface for sampling. A previously connected hand pump and sample bottle assembly was used to suction water from the surface of the water table into the sampling bottle. Sixty milliliter samples were taken from each well including the lake well and returned to the laboratory for immediate analysis. The upper well was a vertical distance of 8 m above the water table. This was a vertical rise greater than a column of water could freely be extracted under gravitational conditions. The sample was thus extracted in portions and composited.

Column Experiments

Sampling of Soils

Intact columns of undisturbed soils were taken at the irrigation site at McCloud Lake. Samples were taken in replicate representing the Candler soil at 0-15 cm and 0-75 cm depths. The soil cylinders were 7.5 cm I.D. diameter polyvinylchloride thickwalled tubing (Schedule 40).

The sampling procedure consisted of carefully and slowly driving the end-sharpened tubes to the proper depth. Since the Candler is a medium sand, there was very little compaction with the 15 cm columns during this operation. When taking the 75 cm columns, the surrounding soil was excavated with depth as the columns were inserted. The columns were driven in close proximity to one another to minimize horizontal soil variation and ease in retraction. Excavation of the columns consisted of digging a pit alongside the battery of columns and carefully laying the columns on their side, lifting horizontally, placing endcaps over the bottom, setting upright, placing endcaps over the top, and labelling for transportation to the laboratory.

Preparation of Sealed Columns

Custom-made endplates with an air entry value of 60 cm were glued onto each end of each column. This was done by setting the column upright on the lab bench, clamping by use of a chain clamp, removing the endcap, carefully levelling the soil surface flush with the column, and using a fine bead of silicone glue with subsequent building of a firm contact surface at the column-endplate joint.

After airdrying for at least 48 hours, the column was saturated by slow gravity flow of deionized water through the bottom of the column to the surface. The endplate tubes were clamped and the column was mounted in a fraction collector.

Elution of Columns

Tygon tubing lines with twist-top plastic connectors were attached to the center port of each endplate to connect the column from the reservoir of treatment solution to the fraction collector tube. A peristaltic pump was placed in the line between the reservoir and the column to provide a constant flowrate of treatment solution to the column. AutoAnalyzer transmission tubing was used in the pump cam assembly. The column was inverted in the collector to eliminate uneven gravity flow, gravity influences, and to minimize any channelling or sideflows within the column. The endplate at the soil surface was then purged of the saturating water using the treatment solution to bring the solution in close contact with the soil surface separated only by the endplate disc. Elimination of all air bubbles was important in this process. The other endplate was likewise purged and air bubbles eliminated using deionized water. (The volume of the endplates and exit tubing to the collector must be known to calculate the pore volumes.) Once the purging procedure was completed, the collector adjusted to activate at the desired volume, and the collection tubes mounted, then the pump was started and collection of the samples proceeded uninterrupted.

Collection of Sample

Solution samples were collected automatically and continuously at timed intervals for specific volumes using a fraction collector Model VL. This was a large temperature-controlled enclosed chamber instrument with a total volume capacity of 3000 mL. Total tube capacity was 20 trays of

20 tubes each tray. Sampling was electronically activated by a sensor which detected a change in intensity of the light beam at the point of interception by the air liquid interface of the rising water column in the sampling tube. Sample volume was preset at 12 mL so that each sample represented 0.1 inch (0.25 cm) acid rain or 10 samples per centimeter of acid rain through the column. Thus for 100 cm acid rain, 400 samples were collected with each tray conveniently representing 2.5 cm acid rain. Continuous head was maintained using a Gilson peristaltic pump Model A which continuously pumped the extracting acid rain solution through the columns and collector at a specified rate of flow.

Treatments

The treatments used were the same as for the field study being acidified lake water at pH 3.0 and pH 3.7 with the control being natural lake water. Thus the acid rain background chemistry simulated exactly that used in the field experiment. The extracting solutions were prepared in plastic 19 L carboys using intermediate solutions of 70.30 H_2SO_4 HNO_3(v/v) and adjusting to the appropriate pH using a Radiometer pH meter Model PRM connected to a combination electrode.

Chemical and Physical Analysis

Preparation and Preservation of Soil Solution Leachates

The leachate samples were taken directly from the field to the lab after careful labelling and sealing in 60 mL plastic bottles. Electrical conductivity and pH determinations were made immediately upon return to the laboratory. The leachate samples were always free of debris from the soil since they had been extracted through the fritted glass discs. Two drops of phenylmercuric acetate (PMA) was added directly upon completion of the pH and EC determinations. This was done to minimize biological processes. Samples were then filtered through a 5 μ membrane, using a syringe and dispensed into 20 mL plastic scintillation vials and labelled, cap and side. Plastic caps with aluminum inserts were not used since Al was to be determined on the samples. In 1982, the within-plot within-depth samples were composited by syringing equal volumes into the vials. The trays of 100 samples each were carefully labelled and refrigerated until further analysis was made

The column leachates were likewise clear when taken from the fraction collection tubes. The EC and pH determinations were made and the samples were then preserved with PMA and then stored for additional analysis.

Parameters

Electrical conductivity

Electrical conductivity was determined using a Barnstead conductivity bridge Model PM FD-C9 with a glass dip cell of K = 1.0

pH

The pH was determined potentiometrically by a Radiometer pH meter Model PHM 64 using a combination electrode

Calcium, magnesium, and zinc

Calcium, Mg, and Zn were determined by atomic absorption spectrophotometry using a Perkin-Elmer Model 460. Calcium was determined using a nitrous oxide-acetylene flame and magnesium and zinc using an air-acetylene flame.

Potassium and sodium

Potassium and sodium were determined by flame emission using a Perkin-Elmer spectrophotometer Model 460.

Sulfate

Sulfate was determined colorimetrically by Technicon Autoanalyzer. The sample was reacted with barium chloride at pH 2.5-3 to form barium sulfate after passing through a cation exchange column to remove metal interferences. Excess barium reacted with methyl thymol blue to form a blue-colored chelate at a pH of 12.5. The uncomplexed methyl thymol blue color was gray; if it was at all chelated with barium, the color was blue. Initially, the barium chloride and methyl thymol blue were equimolar and equivalent to the highest concentration of sulfate ion expected, thus the amount of uncomplexed methyl thymol blue, measured at 460 nm, was equal to the sulfate present.

Aluminum

Aluminum in dilute solutions buffered at pH 6 reacted with Eriochrome Cyanin R dye to produce a red to pink complex which exhibited maximum absorption at 535 nm. Aluminum was determined by Technicon Autoanalyzer.

Nitrate-nitrogen

The automated procedure utilized the reaction whereby nitrate was reduced to nitrite by a copper-cadmium reduction column. The nitrite ion then reacted with sulfanilamide under acidic conditions to form a diazo compound. This compound then coupled with N-1-napthylethylenediamine dihydrochloride to form a reddish-purple azo dye.

Ammonium-nitrogen

The automated procedure utilized the Berthelot reaction in which the formation of a green colored indophenol compound occurred when the solution of an ammonium salt was added to sodium phenoxide followed by the addition of sodium hypochlorite. A solution of potassium sodium tartrate was added to the sample stream to eliminate the precipitation of the hydroxides of the heavy metals which may be present.

Phosphate-phosphorus

The automated procedure utilized the molybdophysphate blue reaction with ascorbic acid as reducing agent.

Chloride

The chloride procedure involved the liberation of thiocyanate ion from the mercuric thiocyanate by the formation of unionized but soluble mercuric chloride In the presence of ferric ion, the liberated thiocyanate ion formed a highly colored ferric thiocyanate complex proportional to the original chloride concentration An automated method (Technicon #99-70W/8) was modified for readout using a scanning spectrophotometer

Iodide

Iodide was determined using an iodide specific ion electrode with a companion reference electrode, both electrodes being attached to an Orion Ionanalyzer Model 901

Soluble organic carbon

Soluble organic carbon was determined using a TOC carbon analyzer Model 826.

Determination of Pore Volume and Dispersion Using Tritium

Since separate columns were used for each of the three treatments for each of the two depths, it was mandatory that the flow patterns or dispersion characteristics be the same for each set If the physics of the water fluxes were not the same from column to column, then differences in the chemistry of the water fluxes would not be necessarily due to treatment differences Column uniformity was readily assessed using Tritium as a radioactive tracer Each column was eluted with a solution of Tritium at 10,000 counts per minute after the completion of the treatment additions. The same procedure was followed for Tritium as for treatment in the use of the collector, except that the saturation procedure was not necessary. Both front and back sides of the breakthrough curves were determined; thus at least two pore volumes had to be collected in the collector. The shape of the curves was not as important as the uniformity among curves, i.e., uniformity of dispersion was more important than degree of dispersion. After the samples had been collected, the tritiated water inside the column was replaced with deionized water, the column dismantled, soil weighed and dried in order to determine the pore volume.

In particular, 1 mL aliquots of the tritiated samples were transferred to scintillation vials and mixed with 16 mL of New England Nuclear Aquasol-2 scintillation cocktail. The samples were counted on a Searle Analytic, Inc., Delta 300 liquid scintillation counter for five minutes. The counts were corrected for background and the pore volumes were corrected for endplate volume and tubing on the outflow.

Soil Sampling and Analysis

Soil samples were collected and composited over plot pre-, during, and post-irrigations from the various depths and analyzed for various physical and chemical parameters to indicate any changes due to acid rain treatment. Soil samples were also taken at various depths to characterize the soil as to cation exchange capacity, extractable acidity, base saturation, components of clay fraction, bulk density, saturated hydraulic conductivity, organic matter, pH, available nutrients by double acid extractant and neutral normal ammonium acetate, particle size distribution, textural analysis, and sand fractions. Soil samples were also taken at 15 cm depth and intervals from the soil, surface to the water table and analyzed for physical and chemical parameters.

Preamble to Results and Discussion

The following Results and Discussion chapter is detailed in the first two sections on ion mobility. It is in these sections that the various combinations of comparisons are made within, between, and among ions, depths, treatments, and years. Summary figures are also constructed to describe the overall relative ion movements for each treatment and depth.

To standardize the comparisons, the terms "within," "between," and "among" are used. These are statistical terms meaning "one," "two," and "three or more," respectively. Their usage might seem monotonous in the text, however, full descriptions are used at each heading to orientate the reader explicitly as to the comparisons being made. This approach also allows stating the means "respectively" without repeating the heading.

Summary tables (Tables 4.13 and 4.15) of the means for field and column data for these sections are given in the fourth section.

To reduce lengthy repetitiveness, the terms "3.0" or "3.0 curve" are used to designate "3.0 pH treatment curve," similarly for "3.7" and "control." In addition, "control" signifies "4.6 pH."

The unit "cm" is used to designate both soil depth, e.g., "15 cm and 75 cm depth" and quantity of added rain, e.g., "45 cm rain."

In the first and second sections, ion mobilities versus increasing rainfall are expressed as curves. These curves are compared in describing the mobilities for the various elements as influenced by treatment and depth. In addition, the means (mg/L) for each curve for each element are given for the various comparisons as a final statement under each section to express the average effect as a figure. These curve comparisons which show the complexity and interrelationships of the ion mobilities are the most interesting aspect of the research both in the field and the laboratory experiments.

In order to compare the relative magnitudes of ion loss, the conversion from mg/L basis to milliequivalents per liter (me/L) basis was performed for the three treatments pH 3.0, 3.7, and 4.6 for each of the two depths 15 and 75 cm.

The third section describes the vertical and horizontal water flow patterns at the field site in the first two parts, respectively. The original scope of the research was to describe ion mobilities as affected by acid rain in the rooting zone of the Candler soil (as given in the first and second sections). However, the positive results and the dynamics of ion mobility increased the interest to investigate (1) vertical soil water movement with depth from the soil surface to the water table, (2) horizontal water movement in the water table zone toward the lake from the plot zone, and (3) the chemistry of the soil water with time in this two-dimensional phase. In order to assess the magnitude of ion losses, it is necessary to know the quantity of soil water loss as well as the concentration of ions in soil solution. In order to obtain the former, the additional experiment as described in Chapter 3

(Materials and Methods) was performed, the results of which are given in this section. The hydrological results were obtained using the neutron probe in the vertical soil profile and the well recorders in the horizontal water table profile. The chemical analytical results were determined over a 14 day period in the vertical profile using soil solution sample tubes and in the horizontal water table profile using vertical wells as sampling sites at various locations between the plot wall and the lake.

The fourth section summarizes in detail the data from the first three sections. These sections are concerned with exchange mechanisms and comparisons of ion movements and losses throughout irrigation periods. However, figures for total loss for each of the various ions for the irrigation periods are required if the magnitude of ion loss (and adsorption) are to be assessed for practical purposes. Total ion losses are expressed as kilograms per hectare (kg/ha) in order to relate to (1) current fertility practices in agriculture and forestry, (2) known losses via plant uptake and cropping, (3) losses by the effect of acid rain compared to the total available ions in the soil, and (4) various other comparisons. Total ion losses are also expressrd as kiloequivalents per hectare (E x 10^3/ha or kEq/ha in some literature) in order to compare cation versus anion losses for mass balance calculations, to relate to H adsorption, and to relate to other literature. Total losses for all major cations and anions are required for meaningful mass balance data. This is why such a comprehensive analytical effort was made. Losses due to the effects of the acid rain treatments can then be estimated by net losses (treatment minus control). In addition, field versus column comparisons can be made. Various other comparisons such as cation loss to cation exchange capacity, changes in base saturation, total loss of cations to base saturation and total exchange, and depletion of exchangeable cations by the treatments can also be made

Mass balance data for total ions both as kg/ha and E x 10^3/ha are also readily calculated showing the magnitude of total ion loss past two depths for the three treatments for field and column. Since sulfate, nitrate, and hydrogen are the major input ions in the acid rain, their adsorption affects the losses of other ions The magnitude of total and net adsorption are calculated for these three ions. Total and net losses for the cations are also calculated and compared to H adsorption. Since Al mobility directly affects root development and nutrient uptake by plants, the magnitude of Al mobilization below 15 and 75 cm depths is of great significance to the plants and has implications for groundwater and lake systems Thus Al mobility and immobilization with depth are calculated for the field and column studies.

One of the objectives was to compare the field and column approach for agreement on ion losses. These comparisons indicate the feasibility of using column studies for estimating field losses Comparisons are made for the pH 3.7 treatment

CHAPTER 4
RESULTS AND DISCUSSION

Field Experiments

1981

Within element, within 15 cm depth, comparison between 3.7 and control (Figure 4.1)

Calcium The 3.7 treatment was consistently above the control. Both curves rose to a peak at the 13 cm rain and slowly decreased. The peaks were 7 and 5 mg/L, respectively, with means being 4.63 and 3.72 mg/L, respectively.

Magnesium The 3.7 treatment was consistently above the control. Both curves rose to peaks at 15 and 20 cm rain, respectively. The 3.7 treatment slowly decreased to 50 cm rain with the control remaining uniformly level. The peak concentrations for the 3.7 and control treatments were 1.75 and 1.0 mg/L, respectively. The means were 1.44 and 0.76 mg/L, respectively.

Potassium The 3.7 treatment was consistently above the control. Both curves were essentially flat in aspect, but very undulating, with no outstanding peaks. The means were 3.24 and 2.74 mg/L, respectively.

Ammonium-nitrogen The 3.7 treatment was generally above the control. The former rose to a peak at 10 cm rain then showed a sharp decrease. The control also rose at the 10 cm rain, with a generally

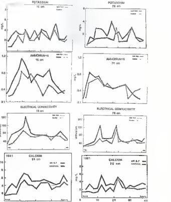


Figure 4 1   Effects of two treatments of 50 cm irrigated acid rain on the movement of ions at two depths under field conditions

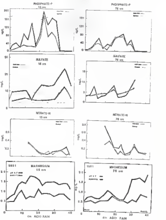


Figure 4.1. Continued.

less steep decrease to 50 cm. The peaks were 1.1 and 0.80 mg/L, respectively, with the means being 0.70 and 0.57 mg/L, respectively.

Sulfate. The SO_4 showed a slow rise to peak at 28 mg/L at 32 cm rain for the 3.7 treatment. The control curve was generally flat, then rose to peak at 35 cm rain at 17 mg/L. Both curves were slightly above the input sulfate concentrations. The means were 17.7 and 9.1 mg/L, respectively.

Nitrate-nitrogen. Both treatments were in close proximity and decreased from 0.4 mg/L to a very low concentration. The means were 0.17 and 0.15 mg/L, respectively.

Phosphorus. The 3.7 treatment was consistently above the control. Both curves exhibited steep increases to peak at 30 cm rain, then decreased precipitously to very low concentrations at the 35 cm. The peak concentrations were 260 and 200 μg/L, respectively, with means being 124 and 60 μg/L, respectively.

Electrical conductivity. The 3.7 treatment was consistently above the control and increased sharply then flattened at a much lower level to 50 cm rain. The control was more uniformly flat in aspect. The peaks were 160 and 70 dS/cm with means of 82 and 62 dS/cm, respectively.

In summary for the cations, Mg exhibited the greatest difference between 3.7 treatment and control on a percentage basis indicating that Mg was indeed affected more than the other cations. On an equivalent basis the order of decreasing dominance was Ca, Mg, K, NH_4-N, and Zn. For the anions, SO_4 far exceeded NO_3-N and PO_4-P regarding treatment differences. This would be expected since SO_4 was the major input ion in the acid rain. Both NO_3-N and Zn showed the smallest treatment difference with control.

The electrical conductivity, the overall ionic strength indicator, showed that the greatest differences between 3.7 treatment and control occurred early in the irrigations and became less distinct with added acid rain. Apparently the 3.7 treatment removed the ions relatively quickly in the irrigation series and the differences disappeared as the soil equilibrated with the 3.7 treatment after the initial flush of ions.

Within element, within 75 cm depth, comparison between 3.7 and control

Calcium. The 3.7 treatment was consistently above the control. Both curves were generally flat with two midpeaks in both curves. The means were 3.23 and 2.27 mg/L, respectively.

Magnesium. The 3.7 treatment was consistently above the control. The 3.7 curve was generally flat until the latter irrigations when it rose sharply and remained high for the duration of the period. The control curve was generally flat throughout but rising slightly with rainfall. The means were 1.09 and 0.65 mg/L, respectively.

Potassium. The 3.7 treatment was consistently above the control throughout the irrigation period, and showed a slow undulating rising curve which again decreased in a concave manner. The control curve remained flat. Means were 1.92 and 1.36 mg/L, respectively.

Ammonium-nitrogen. Although both curves were in close proximity, the 3.7 treatment was slightly above the control at the early irrigations, then decreased to below the treatment during the latter irrigations. Both decreased from a high initial level of 0.8 mg/L. Means were 0.55 and 0.52 mg/L, respectively.

Sulfate. Both curves were essentially flat with undulations, especially for the 3 7 curve. Although the data were not complete, there was a rising tendency at the latter irrigations, as in the 15 cm curves. Means were 5.6 and 4 9 mg/L, respectively, both below the input SO_4 concentrations, thus indicating sulfate adsorption.

Nitrate-nitrogen. Both curves showed similar sharp decreases and were in close proximity. Means were 0.30 and 0.19 mg/L, respectively.

Phosphate phosphorus. Both the curves were in close proximity indicating little treatment effect at 75 cm depth. The means were 0.044 and 0.036 mg/L, respectively.

Electrical conductivity. The curves showed less difference in treatments at the 75 cm depth than at the 15 cm depth. Although there was an initial discernible difference between treatments, especially with two early peaks which corresponded to increases in Ca, Mg, and K, the curves for this depth were essentially in close agreement.

In summary, the same conclusions can be drawn for the 75 cm depth as for the 15 cm depth. The most striking treatment difference was with Mg during the latter irrigation when there was a precipitous increase in Mg. This could be explained by the movement in a delayed fashion of Mg from the surface 15 cm to the 75 cm depth with increasing rain additions. On an equivalent basis, Ca showed the greatest difference between treatments, followed by Mg, K, and very little differences noted for SO_4, NO_3-N, Zn, and PO_4-P.

Within element, within 3.7 treatment, comparison between 15 and 75 cm depths

Calcium. Both curves were similar, rising during the early irrigations and decreasing slowly to 50 cm rain. The Ca was higher in the 15 cm depth than at 75 cm depth. Means were 4.63 and 3.24 mg/L, respectively.

Magnesium. The curves were very dissimilar indicating that the movement patterns of Mg were depth dependent. The 15 cm curve showed a sharp rise early in the irrigation period and a slow decrease to 50 cm rain. The 75 cm depth curve showed a flat uniform curve with a sharp rise in the latter irrigations. This indicated a net movement of Mg from the upper to lower portion of the profile for the 3.7 treatment. Means were 1.44 and 1.08 mg/L, respectively.

Potassium. Both curves were undulating, which appeared to be a typical pattern for K. The 15 cm curve was less concave and higher in concentration than the 75 cm curve. Means were 3.23 and 1.92 mg/L, respectively.

Ammonium-nitrogen. Although the 15 cm curve was higher in concentration than the 75 cm curve, both curves exhibited similar patterns. Both increased sharply and steadily decreased to baseline again at 50 cm rain. Means were 0.69 and 0.55 mg/L, respectively.

Sulfate. The curves were dissimilar. The 15 cm curve rose steadily and uniformly to high concentrations. The 75 cm curve remained low and essentially flat, never approaching the input SO_4 concentration. This indicated initial mobility of the sulfate to below 15 cm depth with subsequent absorption above the 75 cm depth. The increase in SO_4 to concentrations above the input concentrations indicated sulfate input from outside sources. The increases occurred during the latter irrigations which was during the summer period. The ambient rainfalls at this period of the year could be carrying increased amounts of sulfur from outside sources. Means were 17.7 and 5.6 mg/L, respectively.

Nitrate-nitrogen. The 15 cm curve was much lower than the 75 cm curve in NO_3-N concentration. This indicated greater natural nitrate accumulation at depth in the Candler. However, both curves decreased with increasing irrigation rainfall which could be due to decreased microbial activity during the summer months. Means were 0.18 and 0.30 mg/L, respectively.

Phosphorus. The 15 cm curve was much higher in concentration of P than the 75 cm depth. This indicated that the exchangeable P was higher in the soil at the surface and was removed by the 3.7 pH rain. There was little P at the 75 cm depth. Both P curves decreased sharply at the latter irrigations. The amount of irrigation that occurred might have depleted the soil of the exchangeable P by the completion of the irrigation period.

Electrical conductivity. The EC curves showed that the ionic strength was higher at the 15 cm than the 75 cm depth. This indicated that there was an overall decrease in the equivalent amounts of ions present as the water moved to the lower depths. Although the individual curves for the elements showed that the cations were indeed moving to below the 75 cm depth, there was a net decrease in ion movement with depth. This could be due to the continual absorption of H and SO_4 in the upper profile. The soil SO_4 cation bridging would also slow the movement of cations to depth. There is probably a point at some depth in the soil profile where there is a net equilibrium point where net movement ceases. However, this would depend to a great extent on the volume and pH of the input water. Large rainfalls could carry the displaced ions to the water table in these porous sands.

Within element, within control treatment, comparison between 15 and 75 cm depths

Calcium, magnesium, and potassium. In all three cases, the control curves were higher at the 15 cm depth, showed a more concave curve, and were more undulating than the 75 cm depth curves. This showed that even the ambient rain continually affected the soil chemistry by continually leaching the cations from the soil upper profile. This must be occurring since the cation concentration in the ambient rain and throughfall is much below that found in the 15 cm soil solution sample. Thus there is continual exchange processes occurring, with subsequent adsorption of the exchanged and removed cations at lower depths in the profile.

Ammonium-nitrogen. The 15 cm and 75 cm curves were very similar in pattern and concentration indicating a more or less uniform distribution of this species with depth. Since the rainfall input was very low, the source for NH_4-N must have been microbial and occurred at the upper cm in the soil. Denitrification was probably also occurring.

Sulfate. There was a higher concentration of SO_4 in the 15 cm than the 75 cm depth. This can be partly explained since the input irrigation rain control had an elevated SO_4 concentration. As the irrigating water moved vertically downward, SO_4 adsorption occurred to lower the concentration at 75 cm depth. In addition, ambient rainfall and dryfall could have contributed to the natural SO_4 input at the soil surface in a continual manner, especially during the summer period.

Nitrate-nitrogen. The 15 cm and 75 cm curves were very similar in pattern and concentration for this ion. This indicated a natural even distribution of NO_3-N in the soil profile. A decrease occurred uniformly regardless of depth as the irrigation period progressed. This could have been a naturally occurring reduction in NO_3-N formation with time, i.e., seasonal fluctuations. The fact that the NO_3-N in the 3.7 treatment was also at the control concentration, despite the elevated NO_3-N concentration in the 3.7 treatment water, indicated possible uptake by plants and microorganisms.

Electrical conductivity. The electrical conductivity curves reflected the increased ionic strength at the upper 15 cm vis-à-vis the 75 cm depth. This was a natural and continual ion movement from the surface, with possible contribution from microbial activity, throughfall, natural additions by dryfall, etc. In addition, the input irrigation water was in the range of throughfall chemistry.

1982

Within element, within 15 cm depth, comparison among 3.0, 3.7, and control (Figure 4.2)

Calcium. The 3.0 curve was consistently above and much higher than the 3.7 and control curves. All curves rose early in the irrigations, indicating the effect that all treatments had on the Ca soil chemistry,

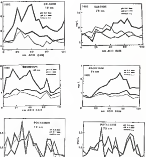


Figure 4-2. Effects of three treatments of 100 cm irrigated acid rain on the movement of ions at two depths under field conditions

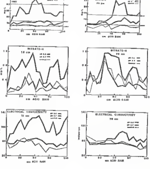


Figure 4 2. Continued

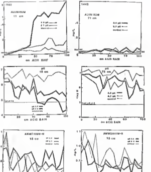


Figure 4.2. Continued

although the control was consistantly below the acid rain treatments. All decreased over the irrigation period. Means were 8.36, 4.56, and 3.49 mg/L, respectively.

Magnesium. The 3.0 curve was much higher and consistently above the 3.7 and control curves. It rose very early in the irrigation indicating rapid displacement of Mg from the exchange sites. The 3.7 was also consistently above the control, the control being essentially flat. Both 3.0 and 3.7 curves followed similar patterns of decreasing magnesium with increasing rainfall. Means were 1.79, 1.02, and 0.77 mg/L, respectively.

Potassium. All three curves were very undulating. Obviously, the different treatments had little effect on the magnitude of K release from the soil exchange sites. There was a slow continual release of K which was independent of hydrogen concentration in the range from 20 to 1000 µeq/L. There was a decreasing trend with increasing rainfall. Means were 1.65, 1.52, and 1.66 mg/L, respectively.

Ammonium-nitrogen. All three curves were very undulating showing a slow decrease with irrigation rain for the 3.7 and control. The 3.0 curve remained high and dominated the latter rainfalls. This would indicate denitrification was occurring since the elevated levels of NH_4-N were resulting from the elevated levels of NO_3-N in the 3.0 acid rain. Means were 0.62, 0.43, and 0.41 mg/L, respectively.

Sodium. Sodium, being in elevated concentrations in the rain irrigation water, showed little difference among the three treatments. The rainfall events were clearly discernible with all three curves moving in unison with increased rainfall. The means for 3.0, 3.7, and control were 3.96, 4.04, and 3.77 mg/L, respectively.

pH. The control curve remained essentially flat and high at a mean of 6.40 for the irrigation period. Both the 3.7 and 3.0 curves dropped steadily as acid rain was applied, the 3.0 curve dramatically so. It was clear that the 3.7 treatment was having a constant effect of lowering the pH of the soil and extrapolations could be made as to the quantity required to approach the critical pH level for Al^{+3} solubility. The 3.0 curve dropped below the soil suspension pH at 4.87 by mid-irrigation period and at 100 cm rain was pH 4.2. The dramatic decrease at the latter irrigations corresponded to an equally sharp increase in Al in the solution. The final pH of the soil leachates at 100 cm rain irrigation were 4.2, 5.2, and 6.2 for the 3.0, 3.7, and control treatments, respectively. This was dramatic, considering that the plot leachates were uniform at pH 6.3 at the commencement of the irrigations. Means were 4.97, 5.55, and 6.40 for 3.0, 3.7, and control, respectively.

Aluminum. All three curves were in close proximity and uniform at a low concentration for the early irrigation period. Thence the 3.0 curve increased sharply and remained at a high concentration during the latter 60 cm of rain irrigations. The 3.7 curve also rose but slowly and less dramatically. The control curve was uniformly low and flat. The dramatic rise of the 3.0 treatment corresponded to a similar sharp rise in hydrogen or a lowering of the pH to a level where trivalent Al entered the system due to a change in the speciation from $Al(OH)_2^+$. This was a significant increase, the concentration being in the highly toxic ranges to plant roots and occurred not too much below the natural pH of the soil at the lake site. However, it is not feasible to expect that rainfalls of this amount and low pH would occur naturally at the site.

Thus observing the curve of the 3.7 treatment would be more reasonable in the short term. Even here, the Al did not increase until 75 cm rain had fallen at 3.7 pH. The peak approached 0.2 mg/L Al which was borderline concentration in soil solution for adverse effects on plant roots. However, the implication was very clear for the effect of specific acid rain events of low pH on releasing an overpowering amount of aluminum to the soil biological system. Means were 1.39, 0.11, and 0.05 mg/L, respectively.

Sulfate. The 3.0 curve was consistently much higher than the 3.7 curve, which was also above the control curve although not so dramatic quantitatively. The 3.0 curve was concave with one large undulation early in the irrigation period. This can be explained by a heavy rainfall that occurred between the irrigation and sampling time interval. Sulfate at 3.0 rose above the input concentration for a short duration then fell below due again to heavy rains at the field site. The 3.7 curve had a similar pattern but rose only slightly above the input SO_4, the peak being delayed compared to the 3.0 treatment, then decreased. The control approached the input concentration and remained uniformly at this level. Thus the curves were similar from this viewpoint. The initial delay in the 3.0 and 3.7 curves indicated that SO_4 adsorption was occurring. Means were 32.2, 11.7, and 7.1 mg/L, respectively.

Nitrate-nitrogen. The 3.0 curve was much higher than the 3.7 curve, which was only slightly higher than the control curve. The 3.0 curve had undulations reflecting the sensitivity of NO_3-N to fluctuations by ambient rainfall. Its mobility and leachability was readily seen in the large trough that occurred at the 50 cm rain period when three large rainstorms leached the irrigation water as a post-irrigation rainfall. Both 3.0 and 3.7 treatments were well below the input concentrations. This indicated rapid uptake, adsorption, or denitrification of the input nitrate. Since the sulfates were being extracted into the sampling tubes near the input concentrations, we can assume that the NO_3-N as determined was indeed the absolute amounts present and that the sampling system was efficient. Means were 0.77, 0.26, and 0.22 mg/L, respectively.

Electrical conductivity. The 3.0 EC curve showed the overall ionic content and reflected the movement closely of the two major ions in the system which were Ca as the cation and SO_4 as the anion on a quantitative basis. The relative effects of the two treatments on the overall movement of ions could be readily seen compared to the control. Means were 106.3, 57.9, and 49.4 dS/cm, respectively.

Within element, within 75 cm, comparison among 3.0, 3.7, and control

Calcium. The three curves originated closely together and gradually separated, with the 3.0 curve increasing as the other curves gradually decreased with rainfall. The 3.0 curve peaked at 8.5 mg/L at 65 cm rain in the irrigation period. The 3.7 curve remained higher than the control curve and peaked at 35 cm rain in the irrigation period at 6.8 mg/L. The control slowly decreased from a peak at 20 cm rainfally of 5.5 mg/L. The 3.0 curve became increasingly dominant with increasing rainfall. Means were 5.55, 4.77, and 3.51 mg/L, respectively.

Magnesium. The pattern of Mg ion movement was similar to Ca, the 3.0 and 3.7 curves peaking later than the control in the irrigation sequence and then decreasing slowly. The control remained uniformly flat and below the 3.7 curve. The peaks for the three treatments 3.0, 3.7, and control were 2.46, 1.20, and 0.89 mg/L, respectively. The 3.0 curve became dramatically dominant with increasing rainfall. Means were 1.51, 0.92, and 0.76 mg/L, respectively.

Potassium. All three curves were very undulating yet exhibited a generally flat aspect with all curves being in close proximity to one another. The effect of the leaching ambient rain period could be clearly seen in all concurrent curves at 50 cm rain, all plots recovering quickly to resupply K.

Ammonium-N. All three treatment curves decreased throughout the irrigations with the control curve undulating widely and dominating the three patterns. The fact that the 3.0 and 3.7 treatment curves showed lower concentrations of NH_4-N at the 75 cm depth than the control indicated that there was increased rapid leaching of the NH_4-N by the increased supply of other cations especially Ca and Mg.

Sodium. Sodium was present in the irrigation rain at a high concentration (4 mg/L). This was unfortunate in one way in that the real sodium mobility could not be determined because of this high external input. However, the constant high concentration of this cation was also an indicator of external influences by observing any fluctuations in the concentration curves. Both the 15 cm and 75 cm curves were coincidal and reflected dilution of the soil solution by rainfall events early and late in the irrigation sequence. Such a curve depression could be used as an indicator of the degree of dilution and the time effect. This could be important if adjustments were to be made for estimating suspected losses via diluting rain water. These losses could readily be seen in the Ca and Mg curves, and are pronounced in the NO_3-N curves.

pH. The 3.0 curve showed a steady slow decline at the 75 cm depth with two precipitous troughs which coincided with the leaching rains that occurred at intervals in the irrigation study. The 3.7 curve coincided closely with the 3.0 curve and both treatment curves were consistently below the control curve which remained relatively flat throughout the irrigation period. The pH troughs in the curves were the result of the hydrogen being leached from the upper surface in the porous sands to the 75 cm depth and beyond. This indicated the rapid response to low pH and intensity of rain over a short period of time, and also the reequilibrium capacity of the sandy soils. The means for the 3.0, 3.7, and control curves were pH 5.92, 6.02, and 6.93, respectively.

Aluminum. All three curves were uniformly low, in close proximity, and flat with some undulations in the later irrigations. The level of Al in solution at 75 cm was obviously very low. This was not unexpected, considering the relatively high pH of the three soil leachate solutions at 75 cm depth. The pH was not low enough for Al^{3+} to dominate the aluminum species. Means were 0.044, 0.044, and 0.030 mg/L, respectively.

Sulfate. The three curves were flat and in close proximity during the early irrigations. Thence the 3.0 curve rose sharply, remained at

22 mg/L SO_4 for three irrigations and decreased to 14 mg/L, remaining so to 100 cm rain. The 3.7 curve rose less dramatically, peaking at 60 cm and later than the 3.0 curve, and then slowly decreased. The control curve was essentially flat. Neither of the 3.0 nor 3.7 curves approached the input sulfate concentrations, while the control did approach its input concentration of 7 mg/L SO_4. The 3.0 curve exhibited sulfate adsorption, the increase at midrange of the irrigations indicating downward movement of the SO_4 from the upper profile as adsorption equilibrium was reached. The decrease thereafter could be the result of heavy rains that occurred at this time in the irrigation sequence, and the soil was recovering as the irrigation period ended. The 3.0 curve showed the same trend, although less dramatically. Means for the 3.0, 3.7, and control treatments were 14.4, 8.3, and 4.4 mg/L, respectively.

Nitrate-nitrogen. Although the 3.0 curve dominated the irrigation period, there was not the difference among the curves that would be expected considering the differing amounts of NO_3-N in the input acid rain. This again reflected losses either to plants and microorganisms, denitrification, adsorption, or natural accumulation at the 75 cm depth in the 3.7 and control plots. The 3.7 and control curves were in fact almost coincident curves indicating nitrate uptake or conversion. This indicated that the NO_3-N in the 3.0 treatment was not completely converted nor absorbed by plant, soil, or microorganism and was moving to below the 75 cm depth although in a decreasing trend. The amount that would reach the water table would depend on the depth to water table beyond 75 cm. The means for 3.0, 3.7, and control were 0.71, 0.44, and 0.45 mg/L, respectively.

Electrical conductivity. The 3.0 EC curve increased gradually to peak at 50 cm then decreased slowly. This high peak coincided with the SO_4, Ca, and Mg peaks, the major ions in the system. The 3.7 and control curves were lower and more flat in aspect reflecting lower ion concentrations in the soil solution. Means for 3.0, 3.7, and control were 88.2, 52.8, and 55.8 dS/cm, respectively.

Within elements, among treatments, comparison between 15 and 75 cm depths (Figure 4.2)

Calcium. For the 3.0 treatment, the 15 cm curve rose higher dramatically to 12.9 mg/L during the first 50 cm rain, then decreased to 6 mg/L. The 75 cm depth curve rose to become slightly dominant above 9 mg/L as the rainfall irrigations continued. This was a classic example of cation movement down the profile. With increasing additions of acid rain, the exchangeable Ca decreased at the 15 cm depth under the acid conditions of pH 3.0. Simultaneously, the Ca was being moved down the profile past 75 cm depth as a cation front. This time-delayed front could then be observed at the 75 cm depth as an increase in Ca in the soil solution at the later irrigations peaking at 60 cm rain at 9 mg/L Ca. As irrigation continued, even the 75 cm depth was becoming depleted of exchangeable Ca as was also the 15 cm depth and the curves both slowly decreased. This pattern cannot be seen as readily for the 3.7 treatment nor in the control. However, both treatments showed the general decrease with rainfall of the Ca levels in soil solution. The lower ionic strength acid rain of the 3.7 treatment leached the Ca less dramatically yet more uniformly in a steady manner over and above the control concentrations. Means for 15 and 75 cm depth for 2.0 pH were 8.36 and 5.55, for 3.7 pH they were 4.35 and 4.77, and for control were 3.49 and 3.61, respectively.

Magnesium. The dramatic movement of Mg can be even more readily observed than for Ca for the 3.0 pH treatment for the two depths. Magnesium rose very quickly at the 15 cm depth to a peak of 2.6 mg/L at 20 cm rain but decreased as the rain continued. Simultaneously, the Mg rose in a steady sloping curve at 75 cm depth to peak at 2.4 mg/L at 50 cm rain. This indicated almost perfect frontal movement, i.e., little adsorption with movement down the profile with gradual depletion of the Mg to a low steady supply concentration. This moving front trend with depth could also be observed clearly for the 3.7 treatment curves but much less dramatically, whereas the control curves were near identical in shape. This indicated that there was a treatment effect and frontal movement even with the less acid treatment. However, the ambient rain (control) showed no differential movement and a stable continual desorption nondifferentiated with depth. Means for the 15 and 75 cm depth for 3.0 treatment were 1.79 and 1.51, for the 3.7 treatment were 1.02 and 0.92, and for the control were 0.77 and 0.76 mg/L Mg, respectively.

Potassium. There was a discernible trend though difficult to observe due to the undulations in the K with irrigation. Generally, the K curves for the three treatments at 15 cm depth were sloping downward with increasing irrigation rain. A flatter aspect could be observed for the three treatment curves at the 75 cm depth. The heavy rainfall period could clearly be observed at 50 cm rainfall in concurrent troughs for both depths for all treatments. Yet the soil continued to supply K at high concentrations at the very next irrigation again for all treatments at both depths. These trends indicated several characteristics for K movement in the Candler soil: (1) that K is exchanged in about equal quantities regardless of depth, (2) that the soil has rapid K re-supplying capacity and fast recovery from leaching rainfall, (3) that K is continually moving down the profile, (4) that treatment had little effect on the magnitude of K leached. Means for 15 cm and 75 cm for 3.0, 3.7, and control treatments were 1.65 and 1.51, 1.52 and 1.49, and 1.66 and 1.76 mg/L, respectively.

Ammonium-nitrogen. The ammonium ion was higher in concentration at the 15 cm than at the 75 cm depth for the 3.0 and 3.7 treatments. At 3.0, the curve for 15 cm depth was undulating, but nearly flat in aspect and remained high compared to the other two treatments. This indicated either a rather constant denitrification or a constant NH_4-N supply by microbial processes separate from the acid rain additions since NH_4-N was in low concentration in the acid rain. It was either adsorbed by the soil microorganisms or plants in the 15 to 75 cm depth or rapidly leached below 75 cm since at 75 cm the NH_4-N was lower in concentration than the 15 cm depth.

The curves for these two depths for the 3.7 treatment were much more similar in concentration than the 3.0 treatment. It would seem that as the acid and nitrate concentrations decreased from 3.0 to 3.7 treatment in the added rain, the ammonium concentration decreased at the 15 cm depth vis-a-vis the 75 cm depth.

In both the 15 cm and 75 cm control curves, the NH_4-N in the natural soil system showed clearly the downward trend with continued rainfall. The sharp undulations in the NH_4-N concentrations coincided for the curves which indicated uniform movement with depth regardless of treatment. The ammonium concentration was higher at the 75 than the 15 cm depth throughout the irrigation period, which was also the case for the NO_3-N. This concentration inversion with depth for these two nitrogen species in the control plots would indicate a natural accumulation with depth. The NH_4-N was lower for the 3.0 and 3.7 treatments at the 75 cm than the 15 cm depth probably due to greater leaching of NH_4-N by the increased and leached cation concentrations of these two treatments.

Means for the 15 and 75 cm depth for the 3.0, 3.7, and control treatments were 0.62, 0.47, 0.43, and 0.35, 0.41, and 0.75 mg/L, respectively.

Sulfate. For 3.0 treatment, although the shapes of the curves were similar, the magnitudes differed greatly between the 15 and 75 cm depth. The SO_4 was much higher in concentration at the 15 cm depth and would be due to the adsorption of sulfate. Sulfate adsorption is pronounced in acid kaolinitic soils which have a pH-dependent charge. Sulfate adsorption was observed in the 3.0, 3.7, and control curves treatments as the percolating rain moved from 15 to 75 cm depth. In only the 3.0 treatment at 15 cm did the SO_4 concentration in the soil leachate increase to above the input concentration in the irrigated rain, and this was only for a short duration for three irrigation events out of 18 total. Thus adsorption and movement down the profile to depth was the dual fate of the SO_4. Means for the 15 and 75 cm depths for 3.0, 3.7, and control treatments were 32.3 and 14.4, 16.7 and 8.3, and 7.1 and 4.4 mg/L, respectively.

Nitrate-nitrogen. The 3.0 curves were quite similar in pattern and magnitude of NO_3-N at each depth. The means were 0.77 and 0.71 mg/L, respectively. However, both 3.7 and control treatments showed higher nitrates at 75 cm than 15 cm depth, the means being 0.26 and 0.44 for 15 cm and 0.22 and 0.45 mg/L for 75 cm, respectively. Nitrate appeared to increase with depth, unlike any of the other ions tested, except for NH_4-N. The 3.7 and control curves clearly showed this. The NO_3-N concentration was so high relatively speaking at the 3.0 treatment that this effect could be masked by the high input concentrations. The concentration inversion with depth for the 3.7 and control could be due to the rapid transport of the nitrate-N from the 15 cm depth range to the 75 cm depth vicinity (which accumulation can be explained later in water transport terms as it affects soil chemistry). The means for 3.0 at 15 and 75 cm depth were 0.77 and 0.71 mg/L, for 3.7 were 0.26 and 0.44, and for control were 0.22 and 0.45 mg/L, respectively.

Aluminum. There was great difference in Al in the 3.0 treatment for the 15 and 75 cm depths and greater than for any other ion tested. Since the buffering capacity of the soil even to a depth of only 5 cm is very great, the effect of added hydrogen cannot be large at depth in the profile, e.g., 75 cm. Since the pH of the soil solution does not decrease below 5.0 at 75 cm, the Al remains as hydroxylated Al (as $Al(OH)_2^+$). Polymerization renders these hydroxyaluminum species essentially nonexchangeable. It is only at the surface that the acid rain exhibited its effects. But it is also at the surface where the bulk of the microorganisms are located and where the plants uptake their nutrients via the roots.

pH The mean pH for the control curves for 15 and 75 cm depth were 5.40 and 6.93, respectively. These correspond to H equivalents of 0.4 μeq/L and 0.1 μeq/L, respectively (i.e., high pH), under which conditions Al would be immobile. The soluble Al concentrations were 0.046 and 0.033 mg/L, respectively. The pH means for the 3.7 treatment for 15 and 75 cm depth were 5.55 and 6.02 (2.8 and 1.0 μeq/L), respectively. Again Al would not be expected to be a problem in plant nutrition and the Al concentrations were 0.112 and 0.044 mg/L, respectively. However, the downward trend at the 15 cm depth for pH and corresponding upward trend for Al are ominous. The soil pH of 4.7 could be projected to be reached for this treatment after 150 cm acid rainfall at which point Al^{+3} would dominate the species. The pH means for the 3.0 treatment for the 15 and 75 cm depths were 4.87 and 5.92, respectively (13.5 μeq/L and 1.2 μeq/L, respectively). The corresponding Al concentrations were 1.39 and 0.044 mg/L, respectively. There was a rapid decrease in pH and corresponding increase in Al for this 3.0 pH treatment near the end of the irrigation period to well above the period mean concentrations for Al and H. Under those conditions, Al^{+3} was freely moving in the soil solution and being leached to depth below the 15 cm with readsorption or immobilization before the 75 cm depth. This has serious implications for the low base saturated, low CEC acid sands.

Electrical conductivity The electrical conductivity, a potentiometric determination, summarizes in a chemical manner what the various individual elements are indicating collectively. The ionic strength of the soil solution decreased greatly as the solution moved from 15 to 75 cm depth. Although it was shown that the cations were moving in greater concentrations to 75 cm, nonetheless, the SO_4 adsorption and H adsorption countered this movement and caused an overall decrease in ionic strength of the electrolyte. Indeed, the sulfate adsorption could be retarding even greater movement of the cations. These differences were not so evident at the 3.7 and control treatments. The means for 3.0 at 15 and 75 cm depth were 106.3 and 66.6 μmhos/cm. The corresponding means for 3.7 treatment were 57.9 and 52.8 and for control were 49.4 and 55.8.

Within 15 cm, within 3.0, comparison among elements

Sulfate was the major ion in the soil leachate throughout the irrigation period. Calcium moved in direct relationship to the sulfate throughout the period but at a somewhat lower concentration. Magnesium was the third highest element in concentration during the first 50 cm of rain and showed a flat curve well below the $CaSO_4$ levels. Then Mg decreased slowly and became less dominant at 60 cm since Al was increasing. Both K and NO_3-N remained uniformly low and flat throughout the irrigation period. Although hydrogen was the ion of lowest concentration, its importance was evident. The H concentration was very low for 50 cm rain then rose sharply by a factor of 10 at the 65 cm rain, levelled until 90 cm rain, and then rose precipitously until at 100 cm rain H was 4th dominant ion in concentration at a pH of 4.19 (64.5 meq/L)

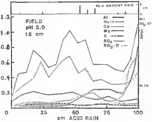
Aluminum was the element in lowest concentration except for H of the seven elements during the first 50 cm rain. Then Al increased slowly to become the third highest element in concentration behind the Ca.SO_4 pair at the 65 cm rain input. At 90 cm rain Al rose again precipitously to become the second dominating ion at 100 cm rain at a concentration of 6.8 mg/L (0.762 me/L). At the completion of the irrigation period, the order of decreasing ion dominance on an equivalent basis was SO_4, Al, Ca, H, Mg, NO_3-N, and K (Figure 4.3a).

Within 15 cm, within 3.7, comparison among elements

At the 3.7 treatment, sulfate was again the dominant ion and was paired closely with Ca and markedly more so than in the 3.0 treatment. Both were at a lower concentration (0.25 me/L). Magnesium was the third dominant element exhibiting a rather flat uniform curve in the 0.08 me/L range. Potassium was the 4th dominant ion throughout the 0 to 100 cm rain followed by Al. Aluminum was flat and uniformly low, whereas NO_3-N exhibited a slowly rising curve at mid-irrigation then decreased slowly to a very low level by 100 cm. The least dominant ion again was hydrogen, although it exhibited a slowly rising curve to 100 cm rain (pH 5.1 or 7.2 μeq/L). The order of decreasing dominance was SO_4, Ca, Mg, K, Al, NO_3-N, H (Figure 4.3b).

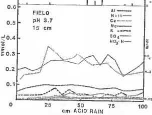
Within 15 cm, within control, comparison among elements

Except for lower concentrations, the sequence of dominating ions followed the 3.7 treatment. There was a slight shift and reversal of



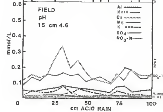
(a) 3.0 pH, 15 cm soil depth

Figure 4.3. Effects of 100 cm irrigated acid rain on the movement of ions under field conditions



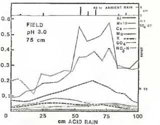
(b) 3 7 pH, 15 cm soil depth

Figure 4 3. Continued



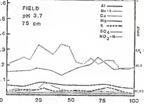
(c) 4.6 pH, 15 cm soil depth

Figure 4.3 Continued.



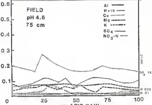
(d) 3.0 pH, 75 cm soil depth

Figure 4.3 Continued



(e) 3.7 pH, 75 cm soil depth

Figure 4.3 Continued



(f) 4.6 pH, 75 cm soil depth

Figure 4.3 Continued.

the Al-N ranking so that the order of decreasing ion dominance was SO_4, Ca, Mg, K, N, Al, H (Figure 4.3c)

Within 75 cm, within treatment 3.0, comparison among elements

Sulfate became the dominating ion by mid irrigation, Ca being slightly higher at the lower soil depths for the first irrigations. The $CaSO_4$ curves were close and uniform in pattern. Magnesium was the third dominating element which exhibited a slowly rising curve to 65 cm rain at 0.2 me/L then slowly decreased to 0.07 me/L at 100 cm. This was well below the Ca concentrations of 0.4 me/L at peak and 0.3 me/L at 100 cm. Sulfate peaked at 0.56 me/L at 78 cm rain. The NO_3-N was the fourth dominant ion almost throughout the irrigation, showing the increase of this ion in the soil solution at greater depth. Potassium was uniformly low and flat, followed by Al and H which were at very low activity. The order of decreasing ion dominance was SO_4, Ca, Mg, NO_3-N, K, Al, and H (Figure 4.3d).

Within 75 cm, within 3.7, comparison among elements

The pattern of ion movement was the same for the 3.7 treatment as the 3.0 treatment at this lower depth of 75 cm. The magnitudes were much lower with the Ca SO_4 curves lying at 0.2 me/L. The only change in the order of dominance was the reversal of NO_3-N and K. The order was thus SO_4, Ca, Mg, K, NO_3-N, Al, and H (Figure 4.3e).

Within 75 cm, within control, comparison among elements

Calcium alone was the dominating element in the soil solution at 0.2 me/L. Sulfate was second in dominance exhibiting a very slowly rising curve, unlike Ca which slowly decreased after a slow rise. Magnesium followed with a flat curve, the sequence being the same as for 3.7 treatment. The order of decreasing ion dominance was Ca, SO_4, Mg, K, N, Al, H (Figure 4.3f). Table 4.13 is a summary (in kg/ha) for the means for all parameters for the 1982 field study at two depths for three treatments, kg/ha = mg/L x 10.093.

1981 vs 1982 (Figures 4.1 and 4.2)

Calcium--15 cm depth

3.7 pH treatment. The curves were similar with both rising early in the irrigations and decreasing slowly, with 1981 curve being flatter. Means for 1981 were slightly higher than 1982, being 4.63 and 4.56, respectively.

Control. Again both controls were of similar magnitude, the curve for 1981 was again more flat than for 1982. Means were 3.72 and 3.49 for 1981 and 1982, respectively.

Calcium--75 cm depth

3.7 pH treatment. Both curves were slightly higher during the early irrigations, but essentially flat. Means were 3.39 and 4.77 for 1981 and 1982, respectively.

Control Large difference in the two years were shown The 1982 concentrations were high compared with 1981, being 3.61 and 2.48, respectively

Magnesium--15 cm depth

3.7 pH treatment. The 1981 Mg concentrations were higher than for 1982, although the curve shapes were similar, both increasing during the early irrigations and decreasing slowly thereafter Means for 1981 and 1982 were 1.34 and 1.02 mg/L, respectively

Control Both curves were similar in pattern and magnitude, means for 1981 and 1982 were 0.76 and 0.74 mg/L, respectively.

Magnesium--75 cm depth

3.7 pH treatment. Both curves showed the pattern of a slow rise to a high peak set of irrigations during the latter period. This indicated the slow movement of Mg from the upper to the lower profile with increasing rainfall, 1981 showing this more dramatically and being slightly higher again than 1982. Means for 1981 and 1982 were 1.08 and 0.97 mg/L, respectively.

Control Both control curves were flat with a slight increasing trend and of similar magnitude Means for 1981 and 1982 were 0.65 and 0.76 mg/L, respectively.

Potassium--15 cm depth

3.7 pH treatment. The 1981 curve was flat with severe undulations. The 1982 curve showed a decreasing trend with rainfall, but also was very undulating, and of lower magnitude than 1981. Means for 1981 and 1982 were 3.24 and 1.52 mg/L, respectively.

Control. The same patterns followed for the control for both years, the means for 1981 and 1982 being 2.74 and 1.66 mg/L, respectively.

Potassium--75 cm depth

3.7 pH treatment. The patterns for the curves both appeared to be concave over the rain period, with the magnitude of 1982 again being below that for 1981. Means for 1981 and 1982 were 1.92 and 1.49 mg/L, respectively.

Control. The curves were similar with both undulating. Means for 1981 and 1982 were 1.39 and 1.76 mg/L, respectively.

Sulfate--15 cm depth

3.7 pH treatment. Curves were different perhaps reflecting the moisture differences for the two years. The 1981 curve showed a rising SO_4 to above the input concentration of 14 mg/L SO_4 at the end of the irrigation period. The 1982 curve approached the input SO_4 and remained flat during most of the irrigation period. Means for 1981 and 1982 were 17.7 and 11.2 mg/L, respectively.

Control. Similar patterns prevailed for the control, but of lower magnitude. Means for 1981 and 1982 were 11.1 and 7.1 mg/L, respectively.

Sulfate--75 cm depth

3.7 pH treatment. Both curves remained below the input concentrations and never did maintain this concentration of 14 mg/L SO_4. Both curves showed increasing slope with irrigation rain. The means for 1981 and 1982 were 5.6 and 8.3 mg/L, respectively, with some data missing for 1981.

Control. Both curves were uniformly low, flat, approaching the input concentration of 7.1 mg/L and of similar magnitude. The means for 1981 and 1982 were 4.9 and 4.4 mg/L, respectively.

Nitrate-nitrogen--15 cm depth

3.7 pH treatment. Both curves decreased with increasing rainfall and were of the same magnitude, the means for 1981 and 1982 being 0.16 and 0.23 mg/L, respectively.

Control. The control curves coincided closely in shape with the 3.7 treatment curves. The means for 1981 and 1982 were 0.13 and 0.21 mg/L, respectively, showing again the slightly greater concentration in the 1982 soil solution N.

Nitrate-nitrogen--75 cm depth

The patterns of the curves for the 3.7 pH treatment and control were similar, showing the same trends as for the 15 cm depth. Again, 1982 was higher in concentration for both treatments. The 1981 and 1982 means for 3.7 pH treatments were 0.26 and 0.39 mg/L, respectively. The means for the control were 0.28 and 0.35 mg/L, respectively.

Table 4 1 shows the concentrations of ions in soil solution for 1981 at three depths averaged over five months comparing the 3.7 treatment with the control treatment The statistics for this comparison for the three depths showed that Ca, Mg, and EC were highly significant (0.01 level) over the control for all depths Potassium, SO_4, and PO_4-P were also highly significant at the 15 cm depth with K and Zn being significant (0.05 level) at the 45 and 75 cm depths Sulfate being highly significant would be expected since SO_4 was added in elevated amounts in the acid rain, yet was not significant at the 75 cm depth, indicating sulfate adsorption Nitrate-N was not significant at the 15 cm or 45 cm depth, indicating loss at the treatment of 3.7 pH, yet was highly significant at the 75 cm depth, a reversal of the sulfate. The 1982 data showed the same trend and indicated an accumulation of NO_3-N at depth as well as uptake and probable conversion at the upper surface depths Phosphorus showed that it was mobile as a result of the acid treatment and was probably associated with the organic matter. Phosphorus was highly significant at the 15 cm depth and significant at the 45 cm depth, with nonsignificance indicated at the 75 cm depth.

Column Experiments 1982

Within Element, Within 15 cm Depth, Comparison Among 3.0, 3.7, and Control Treatments (Figures 4 4, 4 5a-c)

Calcium

The 3 0 curve for Ca rose sharply to a peak at 15 cm rain at 12 5 mg/L Ca Then there was sharp decline to the 100 cm rain at 2 mg/L Ca

Table 4.1 Effects of two treatments of 60 cm acid rain on the movement of ions at three depths under field conditions

Treatment	Depth (cm)	DC	Mg	Ca	K	Zn	NH_4-N	SO_4	NO_3-N	PO_4-P	pH
		μmhos	mg/L				mg/L			μg/L	
Acid rain pH 3.7	15	81	1.35	4.92	3.06	0.48	0.70	17.7	0.17	124	6.64
	46	69	1.19	4.49	2.49	0.44	0.57	--	0.20	62	6.90
	76	62	1.03	3.57	2.08	0.42	0.55	5.6	0.26	44	6.89
	$\bar{x}$ o/depth	71	1.20	4.32	2.54	0.45	0.61	11.7	0.21	85	
Control rain pH 4.7	15	61	0.75	3.84	2.53	0.56	0.57	11.2	0.13	60	6.86
	46	52	0.69	2.52	1.89	0.41	0.49	--	0.24	34	6.85
	76	48	0.64	2.47	1.41	0.37	0.52	4.9	0.20	38	6.74
	$\bar{x}$ o/depth	54	0.69	2.96	1.94	0.45	0.53	8.0	0.19	57	
Acid rain vs. control rain ± %	15	+33	+80	+28	+21	-14	+23	+59	+31	+207	-4
	46	+33	+72	+75	+32	+7	+16	--	-17	+86	+1
	76	+29	+49	+45	+48	+14	+6	+14	+30	+16	+2
	$\bar{x}$	+31	+74	+46	+31		+15	+39	+15	+49	
Acid rain vs. control rain t-test	15	3.66**	11.05**	4.71**	5.13**	2.06ns	2.70*	4.89**	1.81ns	4.60**	1.07ns
	46	4.63**	8.58**	8.24**	2.14*	2.23*	0.79ns	--	1.05ns	2.50*	1.53ns
	76	3.04**	5.63**	4.72**	2.63**	2.96*	0.50ns	1.30ns	2.53*	1.43ns	ns

**significant at 0.01 level

*significant at 0.50 level

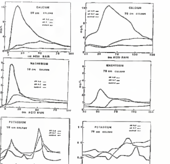


Figure 4 4. Effects of three treatments of 100 cm applied acid rain on the movement of ions in 15 and 75 cm soil columns.

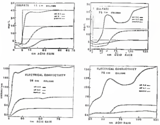


Figure 4.4. Continued.

The 3.7 curve showed a steady incline to peak at 45 cm at 3 mg/L and thence a slow decline to 100 cm at 2 mg/L Ca. The control curve was essentially flat and low at 0.4 mg/L. Means were 4.32, 1.74, and 0.71 mg/L, respectively.

Magnesium

The 3.0 curve rose sharply to peak at 5 cm at 6 mg/L and sharply declined to 25 cm at 2 mg/L thence a slow decline to 1 mg/L Mg. The 3.7 curve rose steadily to peak at 15 cm rain at 1.7 mg/L and declined very slowly to 100 cm at 1.2 mg/L Mg. The control curve slowly rose to 0.7 mg/L and remained a flat curve to 100 cm rain. Means were 1.45, 1.17, and 0.70 mg/L, respectively

Potassium

Potassium exhibited two distinct peaks in its curve for all three treatments and all occurred concurrently at 20 and 60 cm rain. All treatment peaks were of similar magnitude in addition, with the second peak being of greater magnitude than the first. Means were 0.79, 0.78, and 0.77 mg/L, respectively.

Sodium

Sodium was the major cation in the irrigation lake water and therefore was a constant input. Thus its movement as effected by acid rain treatments in the soil could not be discerned readily regarding magnitude.

The three treatments did differentiate in the time sequence of sodium replacement from the soil. The pH 3.0, 3.7, and control treatments showed the peak to occur at 3 cm, 7 cm, and 12 cm, respectively, indicating a rapid release of the soil sodium. Means were 3.27, 3.26, and 3.02 mg/L, respectively.

Sulfate

The sulfate was the major anion and thus major input onto the soil. The 3.0 curve, having a SO_4 concentration of 41 mg/L, showed a rapid rise to 38 mg/L at 5 cm rain, a levelling off until about 20 cm rain, then approaching the input concentration and remaining steady at this level. The 3.7 curve showed a similar but less dramatic rise to the input concentration at 14 mg/L at 15 cm rain and remaining steady at the input concentration. The control curve was even less dramatic, approaching the input concentration of 7 mg/L SO_4 at 25 cm rain, after a fairly rapid incline to 13 cm rain. Means were 39.0, 11.9, and 5.6 mg/L, respectively.

Hydrogen

The 3.0 curve for H consisted of two plateaus, the first plateau at about 25 µeq/L (pH 4.6) and extending to 10 cm rainfall. The second extensive plateau extended from a rising curve from 20 to 70 µeq/L (pH 4.15) over the 10 to 50 cm rain period. Then the H levelled off at 72 µeq/L. This dual-plateau curve can be explained in exchange mechanism terms vis-à-vis the other cations. The 3.7 curve was similar in pattern to the 3.0 curve, but at a lower magnitude of H. The first small plateau occurred at 10 µeq/L (pH 5.0) and the second at 30 µeq/L (pH 4.52). The control curve showed three plateaus, the latter extending from 40 cm to 100 cm rain in the 15 µeq/L (4.8) pH range. This, by no coincidence, was the pH of the natural soil solution indicating that the control column stabilized regarding H after 40 cm rain at the natural pH, the 0 to 40 cm rain showing H adsorption (which coincided with cation desorption). Means were 4.10, 4.54, and 4.89 pH, respectively.

Aluminum

The Al curves for all three treatments were uniformly low to 15 cm rain, then the 3.0 curve rose steadily and uniformly to 10.8 mg/L Al at 50 cm rain. This was an increase of more than 100-fold for this important element. The 3.7 curve remained low with the control curve being very low in Al at trace concentrations. Means were 5.73, 1.33, and 0.30 mg/L, respectively.

Nitrogen

The NO_3-N curve for 3.0 treatment showed the highly mobile nitrate ion to rapidly move through the soil, the curve rising sharply and immediately after irrigation commenced. There was a slight delay before the leachate concentration rose to equal the input concentration. This indicated some adsorption or uptake of nitrate ion. The 3.7 curve was similar in aspect but of lower magnitude, the curve also reaching the input concentration early in the irrigation series. The control was uniformly low and at trace amounts, as was the nitrate-N in the input rain. Means for 3.0, 3.7, and control were 1.85, 0.20, and 0.05 mg/L, respectively.

Chloride

The chloride curves were all uniformly at the input concentration and uniform in shape, chloride being a mobile ion and present in relatively high concentrations in the irrigation rain. Means were 8.3, 9.1, and 6.9 mg/L, respectively.

Electrical conductivity

The EC curve for 3.0 rose sharply and immediately after the irrigations commenced (past the 1st pore volume). The rise coincided with the Ca, Mg, SO_4 as the major ions in the soil system. The slight peak depression at about 20 cm reflected the commencement of the rapidly decreasing post-peak trend for the cation concentrations. Had it not been for the increasing rise of the SO_4, the trend would have continued. However, the SO_4 concentration moved the curve even higher to remain there as the H, then the Al increased. The exchange mechanism, though dynamic with respect to individual ions, nonetheless had reached a plateau when considering the dynamics of the total ions, at about 150 dS/cm. This was about 34% of the input of 446 dS/cm. Obviously, at 100 cm rain, the soil was still adsorbing 66% of the ionic activity of the input ions.

The curve for the 3.7 treatment was similar, but lower in magnitude than the 3.0 curve, peaking at 75 dS/cm. The control followed a similar pattern peaking at 42 dS/cm. Means were 142, 68, and 41 dS/cm, respectively.

Within Element, Within 75 cm, Comparison Among 3.0, 3.7, and Control (Figures 4.4, 4.5d-f)

Calcium

The 3.0 curve showed a slow rise from 4 mg/L to 5.5 mg/L at 15 cm, then a sharp increase to 12.5 mg/L Ca at 35 cm rain, then a sharp steady decline to 3.5 mg/L Ca at 100 cm rain. The 3.7 curve was much lower and rather flat until 35 cm, then a slow increase to 4 mg/L at 100 cm rain. The control curve was essentially flat throughout the 100 cm rain at 2 mg/L Ca. Means were 6.86, 2.72, and 1.71 mg/L, respectively.

Magnesium

Magnesium increased sharply to 3 mg/L at 20 cm, then decreased sharply to 1.75 mg/L at 35 cm, flattening out to 100 cm at 1.3 mg/L Mg. The 3.7 curve was flat until 30 cm, then a sharp incline occurred to 1.5 mg/L and remained steady to 100 cm. The control curve was flat for the 100 cm at 0.5 mg/L Mg. Means were 1.35, 0.91, and 0.42 mg/L, respectively.

Potassium

The 3.0 curve showed a slow rise to 65 cm at 0.7 mg/L K and a flattening of the curve to 100 cm at 0.6 mg/L K. The 3.7 curve showed a similar pattern, lower in magnitude, but rising at 100 cm to 0.7 mg/L. The control curve was undulating but essentially flat at 0.2 mg/L. Means were 0.60, 0.55, and 0.42 mg/L, respectively.

Sodium

The sodium for the three treatments followed a similar pattern as for the 15 cm, with the peaks rising in order of 3.0, 3.7, and control, respectively, all to become level at 3.5 mg/L Na. Means were 3.32, 3.06, and 2.80 mg/L, respectively.

Sulfate

The 3.0 curve exhibited two sharp inclines along its path. One occurred at 30 cm, peaking at 25 mg/L SO_4. The second incline commenced at 65 cm and increased to the input concentration of 41 mg/L SO_4 at 100 cm. These two troughs in the curve indicated adsorption:desorption phenomena which corresponded to the movement of the cations. The 3.7 curve remained flat until 30 cm, then rose sharply to 13 mg/L SO_4 at 45 cm rain and remained flat to 100 cm, never reaching the input concentration of 14 mg/L SO_4. The control curve also remained flat until 30 cm and rose to the input concentration of 7 mg/L and remained steady until 100 cm rain. These curves also exhibited sulfate adsorption reactions. The means were 22.2, 8.3, and 4.8 mg/L, respectively.

Hydrogen

The 3.0 curve exhibited a slowly decreasing incline to 50 cm, then a steeper incline from 20 μeq/L (pH 4.7) to 70 μeq/L (pH 4.1) at 100 cm rain. The 3.7 curve remained essentially flat at 10 μeq/L (pH 5.0) with a slight depression to 5 μeq/L (pH 5.3) in the 20 to 25 cm rain period. This was the period when Ca and Mg were being displaced as H was being preferentially adsorbed, thus exhibiting a decrease in H exiting from the column, and therefore a rise in pH for this duration. The control curve showed a slow but low rise to peak at the 100 cm rain at 7 μeq/L (5.2). Means for 3.0, 3.7, and control treatments were 28 μeq/L (pH 4.55), 6.1 μeq/L (pH 6.09), and 5.4 μeq/L (pH 5.27), respectively.

Aluminum

The 3.0 curve for Al was very low and flat until 50 cm rain, then exhibited a very steep incline to 65 cm at 1.2 mg/L Al and slowly increased to 100 cm rain. The 3.7 and control curves were low and flat throughout the irrigation period. Means were 2.60, 0.25, and 0.17 mg/L, respectively.

Nitrogen-N

The nitrate-N curve for the 3.0 treatment showed a sharp rise to the input concentration of 2.33 mg/L, exhibited a steep trough at 20 cm, and thenrose again more slowly to the input concentration at 100 cm rain. The depression occurred when other ion activities were rapidly changing and coincided with the H depression. The 3.7 and control curves exhibited concentrations at the input level of 0.54 and 0.04 mg/L, respectively. Means were 2.09, 0.47, and 0.04 mg/L, respectively.

Chloride

The chloride curves for 3.7 and 3.0 were at the input concentration after a very sharp rise. The control curves exhibited a slow rise after initial adjustment. Means were 12.2, 10.0, and 8.0 mg/L, respectively.

Electrical conductivity

The EC curve for 3.0 was a slowly undulating curve which appeared very much like the sulfate curve. The 3.7 and control curves were also similar in appearance and slope sequence. Since sulfate was the major ion in the system this was not unexpected. However there were modifications affected by the activities of the displaced ions. Means were 111, 46, and 36 dS/cm, respectively.

Within Element, Within 3.0, Comparison Between 15 and 75 cm Depths (Figures 4.4 and 4.5a-d)

Calcium

Calcium peaked at 15 cm rain in the 15 cm depth and at 35 cm rain in the 75 cm depth, showing a delayed front in the deeper profile. Both peaks were at 12.5 mg/L indicating a constant moving front at 12.5 mg/L down the profile, or an adsorption-desportion of equal proportions as the Ca moved down the profile. Both curves declined smoothly and rapidly from their respective peaks to 100 cm rain. Peaks were 1.5 mg/L for the 15 cm depth and 3 mg/L for the 75 cm depth. There was a much greater total Ca movement from the 75 cm depth than from the 15 cm depth. Means were 4.32 and 6.86 mg/L, respectively.

Magnesium

The magnesium curves exhibited a similar sequential release of Mg from the exchange sites, but there were two important differences. The 15 cm depth Mg peak was at 5 cm rain and for the 75 cm depth was at 20 cm rain. The peak for the 15 cm depth was 5.5 mg/L, with the peak for the 75 cm depth at 2.8 mg/L. This indicated a slower but more uniform desorption with depth and some adsorption in the 15 to 75 cm depth. Means were 1.45 and 1.38 mg/L, respectively.

Potassium

Potassium in the 15 cm depth curve showed the twin peaks at 10 cm and 60 cm rain. In the 75 cm depth, the K was of lower magnitude throughout, the high corresponding peak delayed by 10 cm rain and less defined, but evident. At 100 cm rain, the 15 cm depth was at 0.5 mg/L and the 75 cm depth was at 0.5 mg/L. This indicated a low steady exchange of K and movement below the 75 cm depth, the sharpness in the 15 cm depth peaks being moderated as K moved down the profile. Means were 0.79 and 0.60 mg/L, respectively.

Sulfate

Both curves were very dissimilar for the 3.0 treatment for the two depths. The 15 cm depth showed some adsorption, but the 75 cm depth showed a pulsing of the sulfate movement with depth and a much more pronounced sulfate adsorption, although both curves were at the input sulfate concentration of 41 mg/L by the 100 cm rain period. Means were 39.0 and 22.2 mg/L, respectively.

Hydrogen

The 3-D curves for the 15 and 75 cm depths were similar in magnitude, but the 75 cm H peak was delayed vis-à-vis the 15 cm H peak. This indicated that the chemistry of H and its reaction dynamics were essentially the same regardless of depth and depth had only a time delay effect causing additional H adsorption in the 15 to 75 cm depth. Any curves between these depths would thus probably be intermediate between these two curves. Means were 4.10 and 4.35 pH, respectively.

Aluminum

The 3-D curves for 15 and 75 cm depths again were similar in shape, but were not similar in time sequence nor magnitude. More Al was passing the 15 cm than the 75 cm depth indicating Al adsorption after initial solubilization at the surface layer. The delay in the sharply rising Al curve of the 75 cm depth was 35 cm rain after the initial rise in the 15 cm depth. Means were 5.73 and 2.60 mg/L, respectively.

Nitrate-N

The nitrate curves were very dissimilar with the 75 cm curve being higher than the 15 cm curve in N concentration. This showed the accumulation of N at depth and was a reversal of the other ions in the system. Means were 1.85 and 2.09 mg/L, respectively.

Electrical conductivity

The 3-D curves showed the total activity of the ions in the soil system as the irrigations proceeded from 0 to 100 cm acid rain. The difference in these two depth curves would indicate the adsorption/precipitation vis-à-vis exchange that occurred. A simple exchange reaction would not be manifested in an overall EC change. Since the 75 cm curve was lower, there was an overall increase in adsorption of ions with depth. This decrease in ion activity was 31 dS/cm since the means for the two depths were 142 and 111 dS/cm, respectively. This was slightly less than the ion activity of the input acid rain of 42 dS/cm which showed the adsorption capacity of the Candler sandy soil.

Within Element, Within 3.7, Comparison Between 15 and 75 cm Depths

Calcium

Both curves were in close proximity, with the 75 cm depth Ca gradually increasing in a slow rise curve over the Ca released in the 15 cm depth. At 100 cm, the 15 cm depth was at 3 mg/L Ca and the 75 cm depth was at 4 mg/L Ca. Thus more Ca was moving from the 75 cm depth than from the 15 cm depth indicating greater movement of calcium with depth at this treatment of 3.7 pH. Means were 1.74 and 2.72 mg/L, respectively.

Magnesium

Magnesium curves for the two depths were very similar in magnitude and pattern. However, the 15 cm depth curve rose quickly at 10 cm rain to 1.9 mg/L and slowly declined to 100 cm at 1.0 mg/L. The 75 cm depth curve increased to the same concentration, but at 45 cm rain, and decreased to 1.0 mg/L at 100 cm. This indicated that at low H^+ concentrations (e.g., at 3.7 pH), magnesium moved in a front down the profile, the peak being about 1.8 mg/L. At higher H concentrations (e.g., at 3.0 pH) there was adsorption with depth. This Mg curve pattern at 75 cm depth was similar to the Ca curve pattern at 15 cm depth. Means were 1.17 and 0.91 mg/L, respectively.

Potassium

The 3.7 curve for the 15 cm depth again showed the twin peaks at 10 and 50 cm rain. As with the 3.0 treatment, these peaks were modified and flattened by the time the solution moved to the 75 cm depth. Nonetheless, the upward climb at the second peak at 50 cm rain could be readily discerned in the 75 cm depth whereas there was a flattening of the curve to 100 cm rain. At 100 cm the 15 cm depth was at 0.9 mg/L and the 75 cm depth was at 0.7 mg/L K. Means were 0.79 and 0.55 mg/L, respectively.

Sulfate

The 3.7 curves were similar in shape but with the 75 cm depth, the SO_4 curve was delayed somewhat and was of lower magnitude, never reaching the input concentration of 14 mg/L. Means were 11.8 and 9.3 mg/L, respectively.

Hydrogen

The 3.7 curves were not similar in magnitude but bore resemblances in shape. Greater adsorption of H was obviously occurring with depth, both curves having stabilized by 100 cm rain at 30 and 10 dS/cm, respectively. Means were 4.54 and 4.94 pH, respectively

Aluminum

The 3.7 curve for 15 cm depth exhibited a slight rising trend to 100 cm rain indicating some Al release by this treatment. The 75 cm curve showed very little Al elevation over the control. Means were 1.33 and 0.25 mg/L, respectively

Nitrate-N

The 15 and 75 cm depth curves were similar in shape and time sequence. However, the 75 cm curve showed a higher NO_3-N accumulation with depth. Means were 0.20 and 0.47 mg/L, respectively.

Electrical conductivity

The 15 cm depth curve was higher in total ion activity than the 75 cm depth curve, again showing a concentration decrease due to adsorption/precipitation of ions with depth. There was a delayed EC rise at 75 cm, but both curves levelled at 65 and 52 dS/cm, respectively. The difference in activity was 20 dS/cm. Means were 66 and 46 dS/cm, respectively.

Within Element, Within Control, Comparison Between 15 and 75 cm Depths

Calcium

Both curves were low and level, the 75 cm depth rendering a more constant and higher concentration of Ca than the 15 cm depth. The concentrations were 2 and 1 mg/L, respectively. Means were 0.71 and 1.81 mg/L, respectively.

Magnesium

The 75 cm depth remained below the 15 cm depth in the concentration of Mg in the soil solution. At higher pH's, Mg did not move increasingly with depth. Apparently under less acid conditions (i.e., pH 4.6), the Mg released from the upper profile was adsorbed to a great extent, with decreased concentration moving below the 75 cm depth. Means were 0.70 and 0.41 mg/L, respectively.

Potassium

The control curve showed that the twin K peaks were evident in the 15 cm depth. These peaks could again be observed to occur in the 75 cm depth, but were greatly reduced, rounded, and delayed somewhat. The peak concentrations at the 15 and 75 cm depth were 0.8 and 0.18 mg/L, respectively. This again showed that under increasingly more acid conditions, potassium moved in greater quantities from the profile. Means were 0.77 and 0.42 mg/L, respectively.

Sulfate

Both curves were similar and rose to the input concentration by 50 cm rain, although the 15 cm curve showed more SO_4 adsorption had occurred. The means were 5.6 and 4.8 mg/L, respectively.

Hydrogen

The 15 cm depth curve showed a greater H concentration than the 75 cm depth curve which indicated H adsorption in the 15 to 75 cm soil depth. Stabilization of the curves had occurred by 40 cm into the irrigation series. Means were 4.99 and 5.10 pH, respectively.

Aluminum

There was a slight elevation in the 15 cm depth Al curve compared to the 75 cm curve, but both were of low magnitude.

Nitrate-N

The 15 cm depth curve showed a slight elevation in this ion over the 75 cm curve. This indicated a natural movement of NO_3-N in the profile. Means were 0.05 and 0.04 mg/L, respectively.

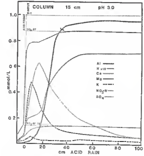
Electrical conductivity

The 15 cm depth curve showed a continual and constant elevation compared with the 75 cm depth. There was a continual adsorption of ion activity with depth showing the capacity of this soil to adsorb ions. Means were 41 and 35 dS/cm, respectively.

Within 15 cm, Within 3.0, Comparison Among Elements (Figure 4.5a)

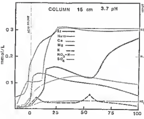
Calcium was the major divalent cation in the system, reaching 0.63 me/L at 15 cm rain and decreasing sharply and steadily to 0.01 me/L at 100 cm. Magnesium was the other major divalent cation in the soil solution system. It rose to its peak before Ca, being at 0.46 me/L at 5 cm rain and decreased similarly as Ca, but remaining at 0.05 me/L at 100 cm rain. The total quantity of Ca removed in the 100 cm rain was greater than Mg. Hydrogen rose to 20 μeq/L (pH 4.7) and remained at this level during the removal of Ca and Mg. At 15 cm rain, as Ca and Mg were beginning to fall precipitously, H again increased sharply, being 40 μeq/L (pH 4.4) at 20 cm rain. It then slowly increased to level out at 45 cm rain at 71 μeq/L (pH 4.15) remaining at that level to 100 cm rain. During this sharp increase in H, Al began to increase even more rapidly so that at 25 cm rain Al was already at 0.8 me/L (7.2 mg/L) and at 50 cm had climbed to 1.2 me/L (11.8 mg/L). Aluminum thus became the dominating cation early in the irrigation period. Potassium remained uniformly low, but was steadily leached from the soil decreasing to a very low concentration at 100 cm.

Sulfate, the major anion in the soil solution, rose quickly at 5 cm and was already approaching the input concentration of 41 mg/L. However, SO_4 decreased slightly at 15 cm, the point where Ca was at its maximum. Then, as the cations decreased, SO_4 again increased and



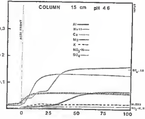
(a) 3.0 pH, 15 cm soil column

Figure 4.5 Effects of 100 cm applied acid rain on the movement of ions



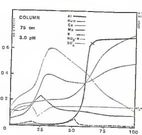
(b) 3.7 pH, 15 cm soil column

Figure 4.5 Continued



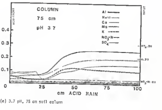
(c) 4.6 pH, 15 cm soil column

Figure 4.5. Continued

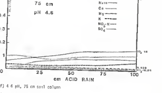


(d) 3.0 pH, 75 cm soil column

Figure 4.5. Continued



(e) 3.7 pH, 75 cm soil column



(f) 4.6 pH, 75 cm soil column

Figure 4.5 Continued

approached the input concentration for the duration of the irrigation period. Thus there was some initial adsorption of sulfate during the period when Ca and Mg were being replaced by H and moving out of the system into soil solution. Magnesium, being more readily removed, exited from the system first, followed by calcium. Since the percent base saturation in these sands is very low (5%), these elements were rather quickly removed, the sites substituted, and hydrogen was free to move through the system. As H increased (the pH decreased), Al species $AlOH^{2+}$ was dehydrolized to become Al^{3+} increasingly as a pH of 4.5 was approached. The sulfate adsorption could have been also a bridge for the Ca which retained this cation preferentially to Mg, thereby accenting the retardation of Ca versus Mg. As the anion sites on the clay and organic matter were quickly occupied by SO_4, SO_4 in solution then began to approach the input concentration of 0.87 me/L SO_4, remaining at this level for the duration of the 100 cm rain application. Nitrate-N increased rapidly to its input concentration of 0.14 me/L.

By the 50 cm rain, the soil solution exchange mechanism appeared to have equilibrated, ion removal becoming static for most ions, and Ca was steadily decreasing and moving from the system. Hydrogen was static and was not approaching its input concentration of 1 me/L (pH 3.0). Obviously, even at only 15 cm rain, there was a great capacity of the Candler sand to continually adsorb the input hydrogen, releasing Al, but not adsorbing the anions SO_4 or NO_3-N. This pattern continued until, even at 100 cm, there was little change, except that Ca and K had essentially disappeared from the system. At 100 cm, the order of decreasing ion dominance was Al, SO_4, NO_3-N, H, Mg, Ca, K

Within 15 cm, Within 3.7, Comparison Among Elements (Figure 4.5b)

At this higher pH, the calcium and magnesium curves approached each other in magnitude, both increasing to 0.13 me/L. However, again, Mg peaked and moved out into the soil solution at 5 cm rain. Calcium increased more slowly and peaked at 45 cm and then slowly decreased to 0.1 me/L. Approximately the same quantity of Ca and Mg were removed by this treatment, the proportion of Ca thus being much less than the 3.0 treatment. During this removal of Ca and Mg, hydrogen was slowly increasing. As Mg peaked and moved out, H increased precipitously to 20 cm rain and levelled off at 28 µeq/L (pH 4.6). This first level occurred as Ca was now being replaced and removed increasingly from the exchange sites. As more Ca was being removed, the H remained at this level of pH 4.5. Since there was a reserve of Ca, hydrogen loss from the column remained stable as the Ca was being removed until at 100 cm, Ca removal had levelled off to 0.1 me/L and was higher than the Mg removal which was now decreasing. During this time when the soil was establishing equilibrium, the Al had likewise increased as H rose above 0.02 me/L. However, unlike the pH 3.0 treatment when H quickly rose to 71 µeq/L, at pH 3.7 the H remained at 0.03 me/L (30 µeq/L). Thus the pH had stabilized at a higher level and Al was not in the form of the trivalent species at this borderline pH of 4.55 for Al^{3+}. In fact, the Al concentration decreased temporarily at 45 cm as Ca peaked in its removal pattern and the pH increased slightly as a result of the increased H adsorption. However, as Ca commenced to decrease in concentration, H again rose, and the Al sharply increased to 0.3 me/L (3 mg/L).

The twin peaks of K could be seen to occur at the point of the Al and H increase, the second peak occurring at the second increase in Al. Sulfate increased in a very similar pattern to the pH 3.0 treatment, again showing some initial adsorption at the period where the cations were being desorbed. At 25 cm rain, sulfate had approached the input concentration of 0.29 me/L (14 mg/L) and remained at this level to 100 cm rain. Thus at 100 cm, the order of decreasing dominance of the ions is SO_4, Al, Ca, Mg, H, NO_3-N, K.

Within 15 cm, Within Control, Comparison Among Elements (Figure 4.5c)

In the control, Ca was not the dominant divalent cation. Magnesium had become the dominant divalent cation throughout the irrigation period (This trend was seen as we progressed from the more acid to the control. At 3.0 pH, Ca dominated the complex, at 3.7 pH, Ca and Mg were in equivalent amounts, at 4.7 pH, Mg dominated the soil solution.) Both curves were relatively level being 0.06 and 0.03 me/L for Mg and Ca, respectively. Hydrogen slowly increased to remain at 19 µeq/L (pH 4.7). Aluminum remained uniformly low at .03 me/L with K having a similar curve pattern but slightly below the Al concentrations. The order of decreasing ion dominance is SO_4, Mg, Ca, Al, K, H

Within 75 cm, Within 3.0, Comparison Among Elements (Figure 4.5d)

Calcium greatly dominated the complex as the major divalent cation. It reached its peak of 0.6 me/L and steadily decreased to 0.08 me/L at

100 cm rain. Magnesium increased in a similar pattern, although peaking slightly before the Ca as the pattern in the other treatments. Magnesium again did not decrease from its peak as rapidly as did the Ca. At 100 cm, the Ca and Mg concentrations were 0.12 and 0.08, respectively. Hydrogen exhibited a low slightly rising long curve from the 5 to 50 cm rain. During the exit of high Ca concentration and other replaced ions, the H ion was being adsorbed and was low concentration in solution. As Ca decreased rapidly commencing at 30 cm, and with Mg also decreasing, the hydrogen increased sharply and uniformly from this 20 μeq/L activity (pH 4.7) to 70 μeq/L (pH 4.14). As the H increased beyond 25 μeq/L (pH 4.6), the Al increased precipitously from 0.02 me/L (0.18 mg/L) to 0.65 me/L (5.9 mg/L) within the rain irrigation of 58 to 68 cm. Aluminum then levelled off and was 0.76 me/L (6.6 mg/L) at 100 cm rain. This indicated the great dominance of Al when the pH reached the pH 4.5 range, which was a reflection of the high percentage of Al on the exchange complex as indicated by the CEC and % base saturation. Potassium again exhibited the twin peaks curve the second and highest K peak arising at 50 cm rain where the pH and Al were increasing.

Sulfate at the 75 cm depth exhibited a behavior unlike the treatments in the 15 cm depth. It exhibited two rising peaks, one at 30 cm, the same placement as the Ca peak, and the second occurring from a slow rise to 100 cm. These peaks were at 0.4 me/L (19 mg/L) SO_4 and 0.7 me/L (34 mg/L) SO_4. There could be some increased adsorption as Ca decreased and moved out of the exchange phase, thus reducing the tendency for removal by ion pair coupling. At the 75 cm depth, the SO_4 never approached the input concentration of 41 mg/L SO_4 (0.65 me/L) and at

100 cm was still only at 0.45 me/L (22 mg/L) which was 52% of the input concentration. Obviously, both hydrogen and SO_4 will be adsorbed for many more cm applications of rain before breakthrough to the input concentrations.

Nitrate-N exhibited a tendency seen in the 15 cm pH 3.7 column, i.e., denitrification. This anion rose sharply to 0.2 me/L (2.8 mg/L) then at 20 cm rain decreased sharply to 0.12 me/L. This could be a clear example of denitrification after initial increase to the input concentration. The order of decreasing ion dominance was Al, SO_4, NO_3-N, Ca, Mg, H, K.

Within 75 cm, Within 3.7, Comparison Among Elements (Figure 4.5e)

Calcium dominated magnesium. However, as with the 15 cm depth, this intermediate pH treatment brought both these ions closer in magnitude. Both exhibited slowly rising curves at 30 cm rain, increasing to 0.19 me/L (3.6 mg/L) at 100 cm for Ca and 0.1 me/L (1.2 mg/L) for Mg. The K curve was uniformly low and flat at 0.01 me/L. Aluminum was likewise low and exhibited a flat curve pattern. Hydrogen decreased somewhat as Ca and Mg rose, then increased to 0.01 me/L at 100 cm. Sulfate was the dominating ion again, but levelled at 0.25 me/L (12 mg/L) not at the input level of 0.3 me/L (14 mg/L). The sulfate curve rose slowly commencing at the 30 cm rain. At 100 cm, the order of decreasing concentration was SO_4, Ca, Mg, NO_3-N, K, H, Al

Within 75 cm, Within Control, Comparison Among Elements (Figure 4.5f)

All the curves were essentially flat and below 0.1 me/L. Sulfate dominated the complex, followed by Ca, Mg, K, Al, and H. The sulfate concentration was at the input level of 0.15 me/L (7 mg/L). Table 4.15 is a summary (in kg/ha) for the means for all parameters for the 1982 column study at two depths for three treatments, kg/ha = mg/L x 10.093.

Within 15 cm, Within N 7.0 NH_4OAc Comparison Among Ca, Mg, K, and Na (Figure 4.6)

A column was also extracted with neutral Normal ammonium acetate to indicate the exchangeable cations, their sequence and magnitude of replacement, and the natural level of exchangeable sodium in the system.

Calcium dominated the complex by peaking at 2.7 me/L (54 mg/L) and decreasing rapidly to 0.25 me/L (5 mg/L) at 16 cm into the irrigation sequence. Magnesium and K all peaked coincidally with Ca, being 1.9 me/L (23.0 mg/L) for Mg and 0.6 me/L (23.4 mg/L) for K. These results showed that Ca and Mg removal by the treatments 3.0 acid rain was in the same ratio as these ions occur on the exchange sites. However, K was also at the same peak concentration and total percentage as Mg, yet was removed by the acid rain in much lower quantities than was Mg. This indicated that potassium was not removed proportionally, being less available than Mg regarding the replacing ability of a very acid rain. Sodium was readily replaced and removed from the soil and peaked at 0.35 me/L (8.1 mg/L). Thus the order of decreasing dominance of the cations on the Candler soil was Ca, Mg, K, and Na.

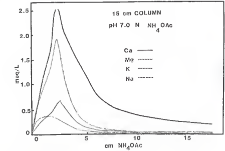


Figure 4.6 Replaceable Ca, Mg, K, and Na in the 0 to 15 cm soil depth of a Candler Typic Quartzipsamment.

Within 15 cm, Within 3.0, Comparison of Flow Rates on Magnitude of Ion Exchange (Figure 4.7)

A 15 cm column was treated with 3.0 pH acid rain at two flow rates, 2.5 cm per hour and 10 cm per hour (which was the rate used in the column experiments). A comparison of the data showed that there was little discernible effect on pH. The EC differences were relatively small. The curves for both pH and EC were identical. However, there was a small difference in the magnitude of the EC once the soil equilibrated. The EC was slightly higher for the 2.5 cm/hr rate compared with the 10 cm/hr rate. This indicated that a solution of slightly higher ionic strength, i.e., higher ionic content, resulted from the lower rate of flow. Thus a slightly higher concentration of the cations and anions could be expected at lower flow rates.

Specifically, when observing the three major cations in the Candler soil, Ca, Mg, and K, the effect was not uniform. Apparently flow rates effect each ion differently. There was no difference in the Ca curves, both peaking at 12.5 mg/L. For the Mg curves, more Mg was extracted with the higher flow rate. The peak for 10 cm/hr was 5.6 mg/L that for the 2.5 cm/hr rate was 4.6 mg/L. However, the shapes of the curves were very similar. In the case of K, the lower rate of 2.5 cm/hr resulted in larger quantities of K being removed from the soil sites. Again, the rate curves were similar.

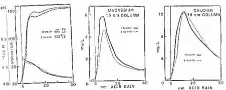


Figure 4.7. Effects of flow rate on the magnitude of ion exchange.

Field Irrigation Experiments on Vertical and Horizontal Flow

Vertical Flux

5 cm rainfall

Figure 4.9 shows the downward movement of irrigation water at various time intervals from the commencement of the irrigation period for the 5 cm rain at 2.5 cm/hr irrigation rate.

At the soil surface, the natural volumetric water content (or resident water) prior to irrigation was 2.2 percent. This gradually increased until at 300 cm the water content was 12 percent. This increase in water content with depth was a normal distribution pattern since there would be decreasing head with depth above the water table surface and a higher percentage of water could be maintained in the water column.

The hourly profile of the vertical water movement showed a decrease at the surface with time. The irrigated water moved in a distinct frontal pattern. Initially, the water was layered horizontally. The two-hour irrigation curve is the profile that existed in the soil at the termination of the irrigation after a 2 hour rainfall at 2.5 cm/hr.

The highest volumetric water content occurred immediately post-irrigation and was 14.3 percent. This occurred at a depth of 30 cm. As the water front moved down the profile, the water content decreased at the surface until at 48 hours it was 4 percent which was nearing the water content at the commencement of the irrigation.

The water front slowed progressively as it moved to greater depths. At 2 hours, the water front had moved 75 cm for an infiltration rate of

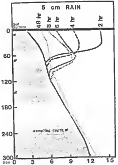


Figure 4.8 Vertical water flux after 5 cm irrigated acid rain.

37 cm/hr At 20 hours, the depth was 200 cm for a rate of 10 cm/hr The decreasing infiltration rate was a result of decreasing head with depth.

As the water front moved to depth yet was above the water table, there was a decrease in the volumetric water content of the irrigated water in the soil profile. This phenomenon would result if the water front was forced to increasingly occupy a smaller percentage of pore space as it moved to depth and increasingly encountered resident water in the larger pore spaces. It was, in effect, running downhill against a gradient of increasing water content which allowed for greater piston displacement.

The amount of water lost to the water table increased with time postirrigation (Table 4.2). At 20 hours, when the moving front was still above the water table, 1670 L had moved to the water table. This water movement must have been by miscible displacement. Thus 44 percent of the volume of water initially irrigated and which was resident water had moved to the water table at 20 hours postirrigation. The vertical movement of the water had slowed to approximately 10 cm/hr. Even if this rate were not to decrease further, the front would not reach the water table until at 38 hours. With a further retardation, it would be near the 49 hour postirrigation period before a breakthrough would occur.

By 48 hours, the water was draining into the water table, the observable front having moved below the 300 cm depth. At this time a volume of water equivalent to 55 percent of the irrigated volume still remained in the soil profile above the water table.

Table 4.2. Water movement above the water table at various times after 5 cm irrigated acid rain

Hours post-irrigation	Irrigation[1] water	Resident[2] water	Total[3] calculated water	Water[4] under curve	Profile[5] water	Water lost to water table	Water lost	Depth of front	Rate of vertical flow
	L						%	cm	cm/hr
2	3785	27441	31226	4265	31707	487	--	75	38
3	3785	27441	31226	3753	31194	320	8.5	90	32
4	3785	27441	31226	3186	30627	599	15.8	120	30
6	3785	27441	31226	2889	30330	896	23.7	135	23
8	3785	27441	31226	2745	30186	1040	27.5	140	18
20	3785	27441	31226	2115	29556	1670	44.1	200	10
48	3785	27441	31226	2070	29511	1715	45.3	385	--

[1] 5 cm rain on plot area of 75 m^2

[2] Initial water content from soil surface to water table

[3] Resident (initial) water plus irrigated water

[4] Irrigated water under the curve

[5] Total water under the curve from soil surface to water table

The 48-hour curve of the soil moisture showed that the initial soil water content was being approached. It would appear that the actual water of a 5 cm rain had little direct effect on the water table within the 48 hour period postirrigation. The indirect effect was to replace initially an equivalent quantity of water and move it to the water table from the near water table zone. Only by a larger rain event, or through subsequent rainfalls, would the majority of the original 5 cm rain be an influence chemically on the water table, i.e., movement of ions from the upper soil region. The data suggested that only approximately 50 percent of the water in a 5 cm rain event actually moved directly to the water table at the specific site location. Assuming a horizontal water table, the closer the proximity to the lake, i.e., shallower the profile, the greater the direct effect of the acid irrigation water on the water table.

7.5 cm rainfall

Figure 4.9 shows the downward movement of irrigation water at various time intervals from the commencement of the irrigation period.

At the soil surface the volumetric water content prior to irrigation was 2.0 percent. This gradually increased to 10.4 percent at 300 cm depth. Thus the resident water content was slightly less throughout the profile than the 5 cm preirrigation water content, although the slope was the same.

Distinct frontal patterns could be readily seen. The 3-hour irrigation curve was the profile of the water front immediately at the

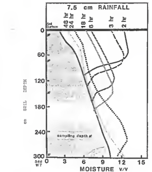


Figure 4 9. Vertical water flux after 7 5 cm irrigated acid rain.

termination of the irrigation of 7.5 cm rain at 2.5 cm/hr, one of the series used in the 1982 irrigations.

As the water front moved to depth, there was a corresponding decrease in the volumetric water content of the soil at the surface. This decreased from a high of 12.6 percent at 3 hours postirrigation to 3.2 percent at 48 hours, which was nearing the preirrigation water content of 2.5 percent. The 3-hour curve showed that the 12.6 percent moisture occurred to a depth of 60 cm, which was twice the depth of the postirrigation curve of the 5 cm rain event for 3 hours. In fact, the water fronts for the corresponding time periods were deeper corresponding to the larger amounts of applied water.

At the corresponding time period, the water front was also moving at a faster infiltration rate than the 5 cm rainfall. At 3 hours, the rate was 37 cm/hr and at 9 hours the rate was 22 cm/hr, which was 60 percent higher than the 5 cm rainfall at the same time period. Although the 5 cm rain had slowed to a rate of 14 cm/hr at 8 hours, the 7.5 cm rain did not slow to this rate until the 21 hour period and at a greater depth. The infiltration rates for the various curves at 110, 140, 190, 205, 285, and 315 cm depth were 37, 35, 27, 23, 14, and 12 cm/hr, respectively. As with the 5 cm rain, there was a decreasing infiltration rate with depth.

The irrigation water content in the soil decreased with time and depth as the water front moved downward. This indicated piston displacement increasing with depth. By 48 hours, the front was draining into the water table. Approximately 32 percent of the equivalent volume of irrigated water remained in the profile after 48 hours, compared to

55 percent for the 5 cm rain. The higher the rainfall, the higher the percentage removal of water to the water table.

It was estimated that despite the 1982 additional liters in the 7.5 cm rainfall vis-à-vis the 5 cm rainfall, the volumetric water content of the 75 m^2 plot to the depth of the water table (4.86 m) was 25000 L compared with 29400 L, respectively. This was due to an initial higher water content of the soil profile prior to the 5 cm rain. At any one time, the water content profile is unique and reflects the daily fluctuations of the water regime in the soil above the water table which are very dependent upon rainfall patterns and intensity and volume of each rain event. Indeed, the water content profile for the 48-hour period for the 5 cm rain showed that there was probably a small ambient rain event prior to the neutron probe readings since the curve showed a bulge near the surface. However, this bulge could also be explained in that the soil surface was relatively drier than the soils at 60 cm due to evaporation and use of water by plants. After a rainfall, there would be a tendency for the soil to retain a larger proportion initially before evaporation depleted the near-surface water content again. This would show up as a bulge in the water curve compared to the initial profile of the dry soil. It must be also stated that neutron readings in the 0-22 cm surface depth are not accurate.

Table 4.3 shows that there was a continual loss of water to the water table almost immediately after the irrigation was terminated. More water was lost to the water table at the various time periods post-irrigation for the 7.5 cm rain versus the 5 cm rain. However, the percentage loss was lower and drainage over the longer period of 48 hours

Table 4 3 Water movement above the water table at various times after 7.5 cm irrigated acid rain

Hours post-irrigation	Irrigation[1] water	Resident[2] water	Total[3] calculated water	Water[4] under curve	Profile[5] water	Water[6] lost to water table	Water lost	Depth of front	Rate of water loss
	L						%	cm	cm/hr
3	5678	23204	28882	5148	28353	529	9.3	110	37
4	5678	23204	28882	5364	28568	314	5.5	140	35
7	5678	23204	28882	5148	28352	530	9.3	190	27
9	5678	23204	28882	4932	28136	746	13.1	200	22
21	5678	23204	28882	4518	27722	1160	20.4	285	14
27	5678	23204	28882	3978	27182	1700	30.0	320	12
48	5678	23204	28882	1845	26049	3833	67.5	385	--

[1] 7.5 cm rain on the plot area of 75 m^2

[2] initial water content from soil surface to water table

[3] resident (initial) water plus irrigated water

[4] irrigated water under the curve

[5] total water under the curve from soil surface to water table

showed that 67.5 percent moved into the water table compared to 45 percent for the 5 cm rain. At 24 hours a volume equal to 30 percent of the rain event was lost to the water table. This was resident water displaced by miscible displacement, since the water front had not reached the water table at this time period. Thus at least 30 percent of the lost water was not irrigation water when the total flux was examined.

The rate of downward movement of the front was greater for the 7.5 than the 5 cm rain and had moved to a greater depth comparatively. It was estimated that about 32 hours were required for the front to reach the water table compared to about 42 hours for the 5 cm rain.

Of more concern from the vegetation standpoint was the quantity of nutrients removed from the root zone. Since soil solution samples were taken from the 15 and 75 cm depths and the concentrations are known over an integrated sampling time of 48 hours, then the quantity of water removed would indicate the nutrients removed below these two depths.

In the case of the 5 cm rain, at the termination of the rain event, only 1150 L or 30 percent of the irrigation water remained in the 0 to 16 cm depth. This decreased to 45 L or 1.2 percent at 48 hours. Thus 98.8 percent of the initial irrigated rain water moved below the 15 cm depth by 48 hours postirrigation for the 5 cm rain.

Data for the 5 cm rainfall in the 0 to 75 cm depth showed that 3771 L or 98.6 percent of the irrigated water remained in the top 75 cm of the soil at the termination of the irrigation event. By 48 hours, 603 L or 15.7 percent remained above 75 cm.

In the case of the 7.5 cm rain event, 729 L or 13 percent of the irrigated water remained in the 0 to 15 cm surface soil. At 48 hours, 81 L or 1.4 percent remained above 15 cm. Thus after 7.5 cm rain, 98.6 percent moved below the 15 cm depth at 48 hours.

Data for 7.5 cm rainfall in the 0 to 75 cm depth showed that 4734 L or 83 percent of the irrigated water remained in the 0 to 75 cm surface soil. After 48 hours, 585 L or 10.3 percent of the irrigated water remained.

Table 4.4 summarizes the data for the two depths for the two rain events.

Since the neutron probe readings were not accurate above the 22 cm depth, the surface soil moisture data were derived from upper extensions of the grid lines from the lower depths. Since the solution samples were taken at 48 hours, only the soil moisture at that time is actually relevant to the chemical analysis. However, it was noted that the soil appeared to stabilize at certain moisture levels at both depths regardless of the amount of rain applied. The percentage of water remaining to that applied would thus differ, but the absolute amount of water in the soil after equilibrium was reached at 48 hours remained approximately the same. If the soil moisture contents were the same prior to the 5 and 7.5 cm rain irrigations, the amount of irrigation water remaining in the 0 to 15 cm layer would be the same regardless of the amount applied. This was equal to 4 percent volumetric moisture for this soil. Since the soil surface 0 to 15 cm averages 3 percent moisture during the normal dry period at the site in Florida, the excess water needed to equilibrate the soil at the 48 hour period was only 0.03 cm rain. Thus 99 percent of any rainfall would move to below 15 cm in this soil.

Table 4.4 Water content in the 0-15 and 0-75 cm soil depths at various times after 5 and 7.5 cm irrigated acid rain.

Irrigation amount (cm)	Depth (cm)	Res-water	Hours postirrigation							Amount applied
			48	20	8	6	4	3	2	
5	15	288	45	135	270	315	531	729	1151	3785
% remaining			1.2	3.6	7.1	8.3	14.0	19.2	30.5	
	75	2493	603	747	1860	2533	2069	3343	3371	3785
% remaining			15.9	19.7	49.1	66.9	81.1	88.3	99.6	
			Hours postirrigation							
			48	27	21	9	7	4	3	
7.5	15	282	81	225	279	360	378	657	729	5678
% remaining			1.4	3.9	4.9	6.3	6.7	11.6	12.8	
	75	2673	585	1044	1404	2178	2727	3908	4734	5678
% remaining			10.3	18.4	24.7	31.3	48.0	68.8	83.4	

For the 75 cm depth, the conditions change since there is a moisture gradient with depth which becomes important in the amount of water held in the soil at any depth relative to that added to the soil, and where soil conditions such as drying are not so influential.

Under average soil moisture content under non-rain conditions for 96 hours, the soil required 60 L (calculated 63 L) per 75 m^2 to equilibrate in the surface 15 cm of soil after 48 hours. The liters required for the 0 to 75 cm depth was 600 L (calculated 594 L) (Table 4.4). Therefore the larger the rainfall, the higher the percentage of irrigation will have passed these respective depths at 48 hours. To calculate quantities of nutrients passing with the irrigating water, a factor can be applied depending on the amount of rain irrigated onto the surface or falling as ambient rainfall. Table 4.5 relates the amount of irrigation water moving past the 15 and 75 cm depth at 48 hours postirrigation to the amount of water applied at the soil surface. These factors can be used to calculate nutrient losses.

38 cm rainfall

A very large rainfall event was imposed on the soil surface of one plot with the expressed purpose of monitoring water table fluctuations. The rate of application was 10.7 cm/hr for a total of 38 cm. Since it was not known if the well level recorders would detect a water table rise, iodide was also added in the irrigation water as a tracer. However, steady state had to first be achieved by an initial irrigation of non-iodide water. Also, the iodide was required to be flushed from the

Table 4.5 Ratio between the amount of irrigation water moving past 15 and 75 cm soil depth at 48 hours postirrigation and the amount of water applied at the soil surface

Irrigation amount (cm)	Soil depth	
	15 cm	75 cm
1.25	.934	.372
2.54	.967	.687
5	.983	.841
7.5	.989	.896
10.5	.992	.928
12.5	.993	.936

system. So, in effect, three rain events totelling 38 cm were applied to the plot surface over a period of 7 hours. Time was required to take soil solution tube samples, well samples, and read the various instruments after each of the three events (Figure 3.6).

Figure 4.10 shows the downward movement of 38 cm irrigation water at the various time intervals from the commencement of irrigation.

At the soil surface, the volumetric water content prior to irrigation was 2.9 percent. This increased with depth to 10 percent at 300 cm. Thus the resident water profile was similar to the profiles of the 5 and 7.5 cm regimes. The mean resident volumetric water contents for the 5, 7.5, and 38 cm rain were 27,100, 23,200, and 21,300 L, respectively. Taking these three as representing average site conditions, approximately 24,000 L of water lie below a soil 3.9 m above the water table over an area of 75 m^2. This approximates 8.3 percent volumetric water content. The soil has a pore space of approximately 45 percent. Thus approximately 19 percent of the pore space is occupied by resident water at any one time. An irrigation of 38 cm rain represents 28,200 L or 119 percent of the volume of the resident water. The 5 and 7.5 cm rainfall events represent 15.8 and 23.9 percent of the resident water, respectively.

The downward movement of the water front of the 38 cm rainfall followed a similar pattern as for the 5 and 7.5 cm events. The 2, 4, and 6 hour curves represent neutron probe readings taken at intervals of 14, 26, and 38 cm of irrigation rain, the 6-hour curve representing the front at the termination of the irrigation total amount applied

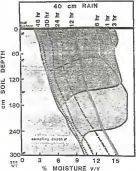


Figure 4.10 Vertical water flux after 38 cm irrigated acid rain.

Although about five times the amount of water was imposed vis-à-vis the 7.5 cm rain event, the volumetric water content did not increase above 17 percent at any one time compared with 13 percent for the 7.5 cm rain. This was despite the rather similar content of resident water and indicated the capacity of this soil to conduct water at a high rate of flow to great depths. The volumetric water content did not increase above 38 percent of the pore volume at any depth. After 48 hours, the water content at the surface 30 cm was 3.3 percent, very close to the content of 2.7 percent prior to irrigation, having decreased from 15.8 percent at 30 cm at the 3-hour period. Thus the 48 hour postirrigation water content was approximately 3 percent after each of 5, 7.5, and 38 cm rain events and very near the preirrigation water content in all cases.

The 3-hour curve for the 38 cm rainfall showed that the water front was at a depth of 190 cm which compared to 60 cm and 30 cm for the 7.5 and 5 cm rainfalls, respectively. Unlike the other two irrigations, the 38 cm rain profile showed a water content that increased with depth by the termination of the irrigation period. The maximum volume of water occurred at 150 cm depth at 9 hours after the commencement of the irrigation. By 12 hours, the water profile had reached, and was draining into, the water table.

As noted earlier, the 38 cm rain was actually three consecutive irrigations of 14, 12, and 12 cm each. Thus the vertical and horizontal distances were exaggerated if compared to a 38 cm continuous rain event. The interrupted fronts can be readily observed as the irrigation water moved to depth in the soil profile. The 4-hour curve showed clearly the 14 and 12 cm rain and the 6-hour curve showed all three rain events, although the peaks were more diffuse. The interirrigation periods can also be seen as sloping decreases in water content in the curves. The three fronts all moved at the same rate with depth as they passed through the soil in three continuous fronts.

A steeper slope was observed on all three curves of the resident water prior to irrigation for the 5, 7.5, and 38 cm rainfalls. These occurred at the 0 to 30 cm depths. The slope could be the effect of evaporation of soil water at the surface due to the high temperatures and also uptake by roots in this zone. This would further decrease the water content (theta) near the surface and be a source of water loss in that direction, i.e., upwards. The rate of frontal movement for the 38 cm rain was much more rapid than for the 5 and 7.5 cm rain events and the rate of water penetration did not decrease as rapidly. The fronts moved to 105 cm after 2 hours for a rate of 52 cm/hr (Table 4.5). It was at 195 cm after 4 hours for a rate of 46 cm/hr and at 295 cm after 9.5 hours for a rate of 43 ch/hr. By 12 hour period, the water was draining into the water table with 41 percent already having been lost to this phase. By 46 hours, only 4.4 percent of the volume of irrigated water remained above the water table.

Figure 4.10 shows that the irrigation front had reached the water table between 9 and 12 hour period. The water was moving at a slightly decreasing rate so that at the water table (3.86 m), the rate would be approximately 45 cm/hr. Thus the front reached the water table in 9.0 hours for a mean rate of 45.2 cm/hr. This compared to 27 hours for the 7.5 cm rain and 33 hours for the 5 cm rain, the mean rates being 14.2 and 11.7 cm/hr, respectively.

If there were no piston displacement, the resident water plus the irrigation water would equal the profile water content at any time before the water reached the water table. The 38 cm rain data indicated that this was not the case and that from the commencement of the irrigation there was a downward displacement and thus movement of the water from above the water table into the water table This occurred on an increasing scale with time within the irrigation. Also, the largest rainfall moved the greatest amount of water into the water table past a given point at a given time As greater amounts of water were imposed on the soil surface, either as rainfalls of long duration at the same rainfall rate or at the same duration but increasing rainfall rate, less of the irrigation water could be accounted for in the water profile curves This indicated that the irrigation water was entering the resident or initial soil water phase and was, in effect, replacing the resident water as the irrigations continued

Prior to the water front reaching the water table, the displacement amounted to about 29.7 percent. Between 6 and 12 hours, replacement figures were 31.1 and 41 0 percent, respectively. Thus the loss at 9 hours would be approximately intermediate assuming that the rate decrease remained constant This was calculated to be 10,200 L which is very close to the profile water content at 2 hours. Apparently, the water moved into the water table immediately as water was applied to the surface of the soil, which was really just a large water column itself. This displaced water continued to move into the water table as the water was imposed on the surface. At 9 hours, when the irrigation front actually contacted the water table, approximately 36 percent of the volume of the irrigated water had moved to the water table. This was not irrigated water, but resident water pushed down by piston displacement.

By 48 hours, only 4.4 percent of the irrigated volume of water remained in the soil profile above the water table. This remaining water, about 1200 L under the plot area, was distributed relatively evenly with depth being approximately 0.3 percent above the preirrigation water profile. The slopes of the profiles at the 48 hour time period were similar for the 5 and 7.5 cm rain events also. At 300 cm, the vertical slopes of the water profiles for 5, 7,5 and 38 cm were 31, 27, and 27 percent, respectively.

The last 4.4 percent water would gradually continue to drain into the water table past-48 hours and revert to the water content of the soil prior to irrigation. If a rain event occurred, the profile would again change depending on the magnitude of the event. The vertical profile of the water content in the soil is a very dynamic one.

The percentage of irrigation water to resident water in the drainage water is of great importance in estimating the loss of nutrients from the soil to the water table.

Moisture release curves for this soil (Figure 4.11) showed that below 6 percent water content, the water was held at high tension. Prior to irrigation, the water content at the 30 cm depth of soil averaged 4.7 percent for 10 of the irrigations for which profiles were determined. The surface water contents were 3.0 percent. Thus the water content near the surface of the soil is held under high tension at most times during the year. In fact, the 6 percent volumetric water content was not encountered until the 120 cm depth was reached on average (180 for

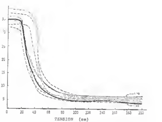


Figure 4.11. Moisture release curves for Typic Quartzipsamment soils on the Central Ridge (Candler soil in dark line)

the 38 cm rain event). This water will move very slowly. Above 6 percent, i.e., below 120 cm, the water will tend to move or be replaced much more rapidly.

The 6 percent deficit occurred above the 180 cm depth for the 38 cm rain event (Figure 4.12). It was calculated to be 3260 L. The water in excess of 6 percent and below the 180 cm depth to the water table elevation was calculated to be 5630 L. This means that 3260 L would move into the higher tension zone pore space upon irrigation and would tend to move more slowly. This represented about 30 percent of the first irrigation sequence of 10,200 L (12 cm rainfall) or 11 percent of the 38 cm rain. The remaining water would be freer to move downward in the profile. Conversely, the water in the soil at depth or above 6 percent could more readily be replaced and moved downward by piston displacement from the upper water moving into the soil pores from above. This amounted to 5630 L, or about 20 percent of the irrigation volume of rain or about 26.4 percent of the resident water. However, there was also a decreasing head with depth which has a decreasing effect relative to water replacement. Thus piston displacement would tend to be very important near the surface of the soil and of decreasing magnitude dependent on the depth to the water table. Since the water table was estimated to be essentially level with the lake at least to 50 meters from the lake edge, the soil surface would theoretically tend to be drier with elevation or distance from the lake edge, other factors such as ground cover, etc., being constant.

Table 4.6 shows the increase in water loss to the water table with time as the water front increased with depth in the soil. At the

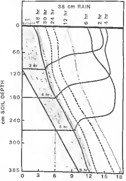


Figure 4.12. Water flux and the movement of various water phases with time to the water table after 38 cm irrigated acid rain.

Table 4.6. Water movement to the water table at various times after 38 cm irrigated acid rain.

Hours post irrigation	Irrigation[1] water	Residant[2] water	Total[3] calc water	Profile[4] water	Water lost to water table	Water[5] under curve	Water lost to water table	Depth of front	Vertical velocity of front	Rate of loss to water table	Rate loss
	L						%	(cm)	(cm/hr)	L/hr	(L/cm)
2	10220	3140	13360	10210	3140	7070	30.7	105	53	1570	29.6
4	19490	6170	25650	20340	5310	14180	27.2	185	46	1328	27.0
6.5	28200	12800	41010	32230	8780	19420	31.1	285	44	1254	29.2
9*	28200	21230	49430	39200	10200	18030	36.0	385	43	1133	28.6
12	28200	21230	49430	37860	11570	16630	41.0	--	(33)	964	
24	28200	21230	49430	31550	17880	10360	63.4	--	(25)	745	
30	28200	21230	49430	25600	23830	4410	84.5	--	(26)	794	
48	28200	21230	49430	22550	26880	1230	95.6	--	(19)	560	

*moving water front reaches water table at 9 hours

[1] 38 cm rain on the plot area of 75 m^2

[2] initial water content from soil surface to water table

[3] resident (initial) water plus irrigated water

[4] irrigated water under the curve

[5] total water under the curve from soil surface to water table

9 hour period when the irrigation water finally made contact with the water table, 10,200 L water had moved into the water table. This had to be resident water and amounted to 48 percent of the resident water. If no water were lost prior to 9 hours, i.e., no displacement, the total water in the profile would be the resident water plus the irrigation water, equalling 49,400 L. With the loss the resident water, 39,200 L remained in the soil above the water table at 9 hours. This represented the maximum amount of water in the soil from the commencement of the irrigation to this period of time of 9 hours. The water thus entered the water table at a rate of 1130 L/hr or equal to a 3.2 cm rainfall. Once contact with the water table was made, the surface profile began to decrease in water content thus reducing head pressure, and the rate of water entry to the water table slowed considerably. The rate of water entry to the water table ranged from 1570 L/hr at 2 hours to 560 L/hr at 48 hours. Thus there was a slow decrease over the 48 hour period of the water movement to the water table.

Table 4.7 shows that all the resident water in the 0 to 115 cm depth was moved to depth by piston displacement. Eighty-six percent of the resident water in the 0 to 190 cm depth profile was removed (or 71 percent of the 115 to 190 cm water). A total of 68 percent of the 0 to 285 cm depth water was removed (or 52 percent of the 190 to 285 cm water). A curve (Figure 4.12) showing these losses and extending to the water table shows that 48 percent of the resident water was lost (or 8 percent of the 285 to 385 cm depth) by piston displacement. The resident water curve in Figure 4.12 represents the resident water remaining in the profile at 9 hours postirrigation. Since drainage of the irrigation water

Table 4.7 Movement of soil resident water to the water table at various times after 30 cm irrigated acid rain

Depth (cm)	Hours	Preirrigation resident water	Water lost to water table	Postirrigation resident water	Resident water remaining
		-----------------	L	-----------------	(%)
0-115	2	3149	3140	0	0
0-190	4	8170	5310	870	13.9
115-190	4	3040	2170	870	28.8
0-285	8.5	12800	8780	4020	31.4
190-285	6.5	6630	3470	3150	47.5
0-385	9	21230	10200	11030	52.0
285-385	9	8400	1420	6980	83.3

into the water table began at this time period, a final estimate is needed for the amount of resident water that would drain to the water table in the 9 to 48 hour period. The hydraulic head had decreased by 12 hours postirrigation and the water content at the surface was not 9 percent moisture, a reduction from 14 percent. Only the water in excess of 6 percent would now readily drain with the irrigation water. This amounted to 2170 L. Thus we have an estimate of the resident water lost from the profile to 48 hours postirrigation. This equalled 10,200 L (the water lost to 9 hours by piston displacement before the irrigation front reached the water table) plus 2170 L free drainage water = 12,370 L or 58 percent of the resident water or 44 percent of the irrigation water. Since at 48 hours, 4.4 percent of the irrigation water remained (1250 L), 46 percent of the total amount of water lost to the water table would be resident water. If the chemistry of the resident water were near the chemistry of the percolating irrigation water, a direct calculation of nutrient loss could be made considering only total volume lost. If the irrigation chemistry were different, a percentage loss of nutrients must be considered. In the case where acid rain events are abnormally low in pH and in effect shock the system, then the percentage effect must be considered since the percolating irrigation water will be high in nutrient. In the present experiments, this was the case. In the future where the present acid rain event will be 3-7, for example, again the system will have stabilized, the resident water will be approximately the same as the percolating irrigation water in chemistry and only the volume loss need be considered in calculating loss of nutrients from the soil.

Horizontal Flux at the Water Table

Figure 4.13 shows the vertical rise of the water table under the irrigated plot as the 38 cm rainfall event drained into the water table. Six wells were located in the transect with well #5 being the plot well. The transect of wells ran downslope with one well being located in the lake itself to be used as a standard reference level. The downslope wells were located 5.6, 16.4, 22.3, and 28.4 m from the plot well and were known as the 6 m, 16 m, 22 m, and 28 m wells, respectively. The 6 m well was located only 1 m from the boundary of the plot itself (Figure 3.7).

There was little indication that nonvertical flow occurred as the water front moved vertically from the surface to the water table. If nonvertical flow had occurred, the graph of the 6 m well recorder would have shown a vertical rise at approximately the same time as the plot well being only 1 m distance from the plot boundary. However, there was a delay of 2 hours before detection of a moving front. This represented a distance of 70 cm with a conductivity of 35 cm/hr established earlier. Therefore there could have been a moving edge of 30 cm or less. Whether this extended angularly to the surface or was just a fringe or capillary front could not be determined since no wells were located directly at the plot boundaries.

Figure 4.13 shows that all four land wells consistently recorded a movement in the water table. These were the plot well, the 6, 16, and 22 m wells. From the well recorder data, the water front reached the water table at about 9.5 hours after commencement of irrigation. The soil depth to the water table was 395 cm which indicated that the

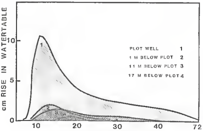


Figure 4.13. Water table fluctuations after 30 cm irrigated acid rain.

water front moved down the profile at an average rate of 45 cm/hr. This was almost the exact rate indicated from the neutron probe vertical profile data (43 cm/hr). The hydraulic conductivity for the soil was 74 cm/hr which shows that the water moved to the water table profile at a rate of about 60 percent of the hydraulic conductivity.

The mounded water peaked at 11 hours postirrigation after a sharp rise from the 8.5 hour detection time, then decreased equally rapidly until at 72 hours the recorded level was at the original water table level. Thus after 72 hours no more water could be detected as draining into the water table, 92 percent having entered the water table by 48 hours.

The total volume of water detected in the plot boundaries at the water table was 10,840 L (or 9850 L at the 48 hour period). A total of 28,200 L was imposed on the plot indicating that only 38.5 percent of the imposed water was detected by the plot well. However, there were no "walls" at the imaginary perimeter of the plot at the water table surface. The soil pores were continuous and water would readily move outside the plot boundaries in all directions or down the gradient. In effect, the water table mounded in spite of the laterally moving water during mounding.

The 11-hour peak represented a 2-hour delay from the time that the vertical front reached the water table. During the 2-hour mounding, water moved laterally. This movement was detected in the downslope wells. The 8.5 hour detection by recorder of commencement of water table mounding coincided closely with the 9-hour estimation from the vertical profile data. Both 6 and 16 m wells recorded a movement at approximately the same time which indicated an initial rapid frontal movement horizontally towards the lake. The time of detection for these two wells was 9.5 hours. Thus by 9.5 hours postirrigation, the water front had moved 385 cm vertically and had created a surface wave response on the water table which was detected another 11.6 m horizontally toward the lake from the boundary of the plot. The total vertical plus horizontal distance of 15.5 m averaged 160 cm/hr.

The plot well peaked at 10.7 cm at 2.5 hours after detection and 11 hours after irrigation commenced. The 6 m well peaked at 2 cm at 2.5 hours after detection and 13 hours after irrigation. The 16 m well peaked at 1.4 cm after 5.5 hours from detection or 15 hours postirrigation. The 22 m well peaked at 0.7 cm at 17 hours, being detected at 15 hours postirrigation.

The peak in the plot well moved to the 6 m well in 2 hours. It travelled 10.7 m to the next well in 2 hours. It moved 6 m to the next well in 2 hours, being now 6 m from the lake. It would contact the lake edge in another 2 hours from the 22 m well, for a total horizontal distance of 28.4 m in 8 hours. This was a horizontal rate of 350 cm/hr. Thus the vertical front moved at an average rate of 43 cm/hr and the horizontal wave front moved at a rate of 350 cm/hr, or 7 times faster than the vertical rate.

The motion of the wave showed that the inplot water table mounded considerably before there was any horizontal movement (Table 4.8). The plot well was at a height of 5.6 cm (50% of peak rise) at 9 hours before any movement was noted at the 6 m well. When the plot well was at its peak, at 11 hours, where vertical movement within the plot equalled

Table 4.8. Water table fluctuations after a 38 cm irrigated acid rain.

Hours post irrigation	Height above water table			
	Plot well	6 m well	16 m well	22 m well
	----------	---------- cm	----------	----------
0	0	0	0	0
7.5	0	0	0	0
8	0	0	0	0
8.5	3.0	0	0	0
9	5.6	0	0	0
9.6	7.9	0.5	0.6	0
10	9.1	0.9	0.7	0
10.5	10.4	1.2	0.8	0
11	10.7	1.5	0.9	0
11.5	10.7	1.7	0.9	0
12	10.4	1.8	1.1	0
12.6	9.7	1.8	1.2	0
12	9.1	2.0	1.2	0
13.5	8.6	2.0	1.2	0
14	7.9	1.8	1.2	0
14.5	7.4	1.8	1.2	0
15	6.6	1.7	1.4	0.05
15.5	6.4	1.5	1.4	0.10
16	6.1	1.5	1.4	0.17
16.5	5.8	1.5	1.2	0.24
17	5.6	1.2	1.2	0.26
17.5	4.8	1.2	1.1	0.26
18	4.6	1.2	1.1	0.19
21	3.6	0.6	0.8	0.14
24	3.0	0.5	0.7	0
27	2.6	0.4	0.6	0
30	2.3	0	0	0
33	2.0	0	0	0
36	1.8	0	0	0
39	1.5	0	0	0
42	1.3	0	0	0
45	1.0	0	0	0
48	0.5	0	0	0
51	0.5	0	0	0
72	0	0	0	0

horizontal movement away from the plot, the 6 m well was at 3/4 peak (Figure 4.14). As the plot well peak was decreasing at 13 hours, the 6 m well was peaking, showing fairly rapid response, and the 16 m well was at 3/4 peak rise. As the plot well peak further decreased, to 3/4 peak at 15 hours, the 6 m well was decreasing to 3/4 peak, the 16 m well was peaking and the 22 m well was beginning to rise. At 17 hours, the plot well was at the same stage as the 9 hours, i.e., about 1/2 peak, the other two well peaks were continuing to decrease, and the front was peaking at the 22 m well. At 21 hours, the well peaks were all below 50 percent peak height and levelling out, thus draining very little additional water at any one well. However, the zone of influence was now extended to 1520 m^2 from the original 75 m^2 area of the plot itself. Thus even a low profile could represent a large total volume of water over the area being drained.

Referring to the 38 cm rain in Table 4.6, at the 12 hour post-irrigation period when the water was draining into the water table, there was a deficit of 11,570 L. This was the difference between the amount irrigated plus resident water and the amount of water under the profile from the neutron probe data. In other words, the water moved into the water table by miscible displacement. At 12 hours, the water content under the profile was 37,860 L, rather than the 49,400 L calculated for no displacement. The deficit can also be readily seen in the well recorder data. The water content under the horizontal profile at 11 and 13 hours was plotted and the 12-hour curves established (Figure 4.14). When transposed to volume, the amount at this time period was 11,600 L, very close to the 11,540 L deficit as seen in the

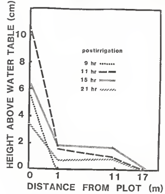


Figure 4-14. Relative rise and fall of the water table with distance from the plot.

vertical profile data. Thus the well recorder data for the water table volume accounted very well for the water deficit noted in the neutron probe data in the vertical soil profile.

Regarding the shape of the four frontal well curves, the plot well curve was definitely a frontal curve and tailed for many hours, showing slow leakage to the water table from the above plot. The 6 m well curve was more bellshaped, and the 16 m well curve was a tailing curve. The 22 m well curve was a small relatively uniform curve.

The rate of peak rise decreased with distance from the plot well. These rates for the plot well, 6 m, 16 m, and 22 m wells, were 3.6, 0.8, 0.25, 0.13 cm/hr, respectively. The rates of peak fall for the four wells were .25, .14, .12, and .09 cm/hr, respectively. The curves showed that with distance from the plot well, the rise-fall curves for the water movement front along the water table surface changed from an initial frontal curve to a tailing curve.

Chemistry of the Vertical and Horizontal Fluxes

Iodide as a tracer for water flow

The 38 cm rainfall was applied in three consecutive rain events. The first 14 cm consisted of lake water to establish steady state flow conditions. This was followed by a 12 cm rain which had a pH of 3.0 using 70:30 H_2SO_4:HNO_3 acids spiked with 10 mg/L of iodide as potassium iodide. This was followed by 12 cm of lake water irrigation to flush the soil system.

Table 4.9 shows the vertical and horizontal movement of iodide and other ions as the water front moved vertically to the water table and the mounded water moved laterally towards the lake.

Iodide background concentrations in the soil profile were very low being 0.018 mg/L averaged from the soil surface to the 300 cm depth where the deepest soil solution sample tubes had been placed. At the 24 hour sampling period after the commencement of irrigation, the iodide was distributed throughout the soil profile with the highest concentrations in the upper 150 cm of soil with a relatively even distribution, the mean being 0.96 mg/L to this depth. The data suggested that the highest concentrations were indeed at or near the 150 cm depth. At 48 hours, the distribution had increased with depth to 300 cm, although the mean concentration had decreased to 0.36 mg/L. At 96 hours and 168 hours (7 days), the even I distribution had been maintained with the mean concentrations decreasing further to 0.190 and 0.097 mg/L, respectively. As the sampling times doubled (1, 2, 4, and 7 days), the mg/L iodide halved, respectively (0.78, 0.36, 0.19, 0.09 mg/L), in the vertical soil profile. This indicated a rapid movement of I to the water table and a continuous dilution concurrently. The iodide rain event had been followed by an equivalent volume of noniodide lake water which could indeed have been the source of the dilution water. It was unfortunate that insufficient leachate was obtained at 19 hours postirrigation for I analysis since the front was moving so rapidly. The well data for this time period indicated that the vertical soil profile was elevated in I above the 0.96 mg/L mean concentration.

Table 4.9 Ion concentrations in the soil solution at various depths and in the water table at various distances from the plot after a 38 cm irrigated acid rain

	Time (hr)	Vertical Distance Soil Depth (cm)					Horizontal Distance Distance from plot well (m)			
		15	75	150	300	385*	6	16	22	28
		dS/cm								
EC (dS/cm)	pre	67	65	146	111	39	35	58	114	43
	19	—	—	—	—	38	35	55	115	42
	24	108	82	139	67	40	55	57	112	42
	48	167	88	132	109	43	45	52	108	45
	7 days	88	80	118	121	51	—	49	105	45
	14d	—	—	—	—	50	—	58	96	45
		mg/L								
Ca	pre	8.9	8.7	14.0	11.1	2.7	1.7	3.4	12.5	1.3
	19	—	—	—	10.3	2.5	2.4	3.1	8.8	1.3
	24	—	—	—	—	2.6	3.8	3.8	12.9	1.3
	48	16.8	18.1	—	17.9	3.0	4.8	3.8	12.7	1.3
	96	13.0	13.0	15.9	14.9	3.6	4.5	4.1	12.4	1.4
	7 d	11.5	12.2	13.6	15.7	3.5	—	4.1	12.4	1.4
	14d	—	—	—	—	4.0	—	4.7	11.2	1.4
Mg	pre	.39	.55	.62	.43	.21	.25	.49	1.96	.83
	19	—	—	—	.38	.23	.42	.56	1.40	.83
	24	—	—	—	—	.25	.35	.55	1.96	.86
	48	1.31	1.41	.90	.66	.28	.30	.53	1.87	.76
	96	.91	1.45	.78	.83	.44	—	.52	1.96	.83
	7 d	.90	1.40	.83	.67	.31	—	.56	1.77	.90
	14d	—	—	—	—	.34	—	.50	1.76	.84
K	pre	.80	.54	1.07	.60	.96	.88	.79	1.02	.35
	19	—	—	—	—	.65	2.45	.67	1.24	.36
	24	—	—	—	1.48	.69	1.97	.71	.87	.38
	48	12.4	3.50	4.0	4.56	.77	1.68	.61	.80	.40
	96	7.42	1.72	15.8	14.9	.75	.99	.75	.71	.43
	7 d	9.8	3.20	14.8	7.42	.81	—	3.92	.97	.45
	14d	—	—	—	—	.90	—	1.26	1.00	.45
Na	pre	2.8	1.5	5.0	4.0	5.3	1.7	2.3	2.2	3.4
	19	—	—	—	—	3.0	1.9	2.3	2.2	3.4
	24	—	—	—	—	3.0	1.1	2.2	2.2	3.5
	48	—	—	—	—	2.9	3.2	2.1	2.0	3.5
	96	—	—	—	—	3.8	1.4	2.2	1.9	3.5
	7 d	—	—	—	—	3.4	—	2.1	1.9	3.4
	14d	—	—	—	—	2.5	—	2.3	1.9	3.4
Al	pre	30	25	40	15	10	95	40	30	90
	19	—	—	—	—	30	90	70	40	95
	24	60	35	55	25	20	75	45	50	90
	48	—	—	—	40	50	85	50	50	90
	96	56	20	70	—	20	80	60	50	95
	7 d	50	30	80	75	10	75	35	40	75
	14d	—	—	—	—	10	—	—	40	90

*depth to water table

Table 4 9. Continued.

	Time (hr)	Vertical Distance Soil Depth (cm)					Horizontal Distance Distance from ploc well (m)			
		15	75	150	300	385	6	16	22	28
pH	Pre	6.52	6 85	7 33	7 41	5 67	6 21	6 41	7.57	4 65
	19	—	—	—	—	5.96	6 30	6 28	6.31	4 65
	24	6.77	6 76	7 11	7 13	5 78	6 13	6 20	6 08	4 66
	48	6.92	6.96	—	7 44	5.44	6 40	6 24	6 02	4 64
	96	6 84	6 80	7 37	—	5.53	6 07	6.11	6 00	4 89
	7 d	6 75	6.79	7 35	7 43	5 70	—	6.37	6.37	4 66
	14d	—	—	—	—	5.41	—	5.14	6 63	4 65
I	pre	.011	008	002	006	017	018	12	128	017
	18	—	—	—	—	022	055	050	15	.036
	24	006	935	1.07	265	037	008	030	030	016
	48	344	397	—	348	034	010	.027	086	014
	96	116	158	350	124	014	075	.016	.071	016
	7 d	212	.090	036	117	118	—	.032	.098	012
	14d	—	—	—	—	006	—	007	012	.009

The wells were also concurrently sampled in order to establish a continuous iodide profile vertically and horizontally at the water table surface. Unlike the vertical soil profile where the iodide was initially evenly distributed as natural background concentrations, the water table well data showed that there was an iodide gradient along the well transect. As the transect approached the lake, the background iodide concentration increased 10-fold from 0.015 mg/L in the plot well to 0.12 mg/L in the 22 m well (4 m from the lake). The lake had an I concentration of 0.016 mg/L. There was thus a zone of high I concentration near the lake. The vertical depth of the soil to the water table at this well was 0.6 m and it is conjecture as to the reason for the elevated I. Subsequent sampling of wells around the lake established concentric rings of I concentration which decreased with distance from the lake. Thus the movement of I in the water table from the plot well to the lake was moving against a natural iodide gradient of considerable magnitude.

From previously, the water front contacted the water table at approximately 9 hours postirrigation and moved toward the lake contacting the lake at 17 hours, peaking at 19 hours. At 19 hours, the I concentration in the 22 m well (the well nearest the lake being 4 m distance) was 0.15 mg/L. This was an increase in the natural concentration and could have been a reflection of the I in the frontal peak, I being very mobile. By 24 hours, this had decreased to 0.03 mg/L indicating a dilution effect. The subsequent sampling periods for this well to 7 days showed that the I remained at this low concentration, the high natural iodide having been diluted by the effect of the unnaturally high irrigation of 36 cm. This well then recovered at 7 days and approached the preirrigation concentration. The data for the 6 m and 16 m wells confirm the elevated I at 19 hours, being well above the background concentrations which themselves were decreasing in these wells being a greater distance from the lake. All the wells were uniformly low during the 48 to 96 hour period indicating that the dilution effect of the irrigation was at a maximum. Thus after an initial flush of I vertically and horizontally along the gradient to the lake, the soil profile and water table surface gradually decreased in I which would seemingly continue to base levels.

Potassium

If iodide could be traced, the counter ion, potassium, should also be traceable in the water system. Table 4.9 shows that the background soil water concentrations at the soil sample tube depths of 15, 75, 150, and 300 cm were relatively uniform and averaged 0.76 mg/L in the soil solution. The 48 hour sampling indicated that K was highest in concentration in the 15 cm depth and uniformly lower at the three lower depths, averaging 6.12 mg/L. Although rather nonuniform, the 4-day and 7-day data for K indicated that the lower depths were highest in K. The average for these two periods were 9.76 and 8.83 mg/L, respectively. The K concentrations in the flux experiment were the highest levels encountered throughout all the previous irrigations, indicating the positive effect of using K as a companion tracer with iodide. Potassium at the 300 cm depth in the plot showed the movement of K to depth with time having peaked at 14.9 mg/L at 96 hours in the sampling sequence chosen. The water table below the plot increased gradually in K concentration as the K slowly moved to depth and was diluted upon contact with the water table.

Potassium movement in the wells corresponded to the iodide data. Again there was an increasing natural gradient as the transect approached the lake, the 22 m well being in the zone of high K, as it was with the I. The lake concentration was 0.35 mg/L of K. The plot well and the 16 and 22 m wells showed depressions in K concentrations with time, respectively. These occurred at 24, 48, and 96 hours, respectively, and would be the effect of the dilution rain. The time profile for the 22 m well clearly showed the depression commencing at 24 hours, the initial front having peaked at 17 hours, with the lowered K continuing to at least 7 days and then showed recovery. The average K in the well transect for the sampling periods showed the initial flush of K as the frontal peak passed the wells, then a decrease in K as the dilution water affected the chemistry and thence recovery.

Most of the potassium obviously moved more slowly down the soil profile than did I due to the lower mobility of K being a cation, although there appeared to be an initial flush of K directly with the front. This movement was also observed horizontally in the water table data. As the mounded water table below the plot moved horizontally and also entered the water table, K gradually increased in concentration and at a slower rate than I in this zone. The 6 and 16 m wells showed the slower movement of K in the water table with distance from the plot. The 16 m well showed that the K increased to well above the background concentration only after 7 days postirrigation, having peaked much sooner in the 6 m well The retardation of the K cation would be expected since the soil was continuous below the water table and K would be continuously adsorbed as it moved into and along this phase of the system

The well upslope from the plot well also showed elevated I and K concentrations at the 7 day samplings. Thus the water table inland from the irrigated plot along the transect was also influenced by the rain event. Since it was previously established that the water table was essentially flat to a distance of at least 50 meters from the lake, i.e., more than 20 meters inland from the plot well, then it would be reasonable to expect mounded flow in all directions from the plot center.

The zone of high ion concentration at the 22 m well formed a chemical barrier. The presence of the ion gradient was not expected and complicated the I and K chemistry. However, this barrier was also a fortuitous occurrence since it offered a standard for observation of the diluting water front that moved towards the lake. Its dilution was as much an indication of rate of flux as was the tracer ions. The K ion, for example, was above 1 mg/L to 19 hours Subsequent samplings showed that the K concentration decreased by 24 hours, was lowest at 96 hours, and at 14 days was again approaching the former levels. This indicated the diluting effect of the irrigation front on the ion gradient and that the front indeed did reach the lake. Iodide also showed the same trend.

Calcium and magnesium

Calcium and magnesium were the two major divalent cations in the soil system The preirrigation soil solution samples showed that Ca increased with depth to 300 cm, whereas Mg remained relatively constant.

The preirrigation means for Ca and Mg were 10.7 and 0.55 mg/L, respectively. During the three postirrigation sampling periods, 2, 4, and 7 days, this increasing concentration with depth was maintained, although the concentrations decreased with time. The means for 2, 4, and 7 days for Ca were 17.6, 14.2, and 13.3 mg/L, respectively.

In the case of Mg, the concentration profile appeared to occur with the 75 cm depth becoming the depth of highest concentration (1.42 mg/L) for the 2, 4, and 7 day sampling periods. Similarly as with Ca, the concentrations decreased with time, although only slightly, Mg being 1.06, 0.99, and 0.95 mg/L, respectively.

In the water table regime, both Ca and Mg showed increasing concentration along the transect with increasing proximity to the lake. The highest concentrations occurred in the 22 m well being 4 m from the lake. The means here for Ca and Mg were 12.3 and 1.81 mg/L. These coincide with the respective concentrations in the 75 cm depth in the soil. For Ca there were two increasing gradients with distance, one in the soil with depth, one in the water table with distance towards the lake, and occurred in both the pre- and postirrigation samplings. For Mg, there was a reverse gradient respective to soil depth, but the water table gradient was the same as for Ca. As Ca decreased with time in the soil at the various depths, it increased in the plot well, the 6 m and 16 m wells. No discernible increase could be seen in the 22 m well in the zone of high concentration near the lake. The same trend was clearly discernible in this well for Mg. Apparently, as these two elements moved down the profile and into the water table, there was a gradual increase in the concentrations in the water table but limited in its extension from the plot boundaries. For Ca, the increase continued to 14 days For Mg, there was an initial increase from the pre-irrigation concentrations, then a gradual decrease which varied directly with the distance from the plot well. In other words, for Mg, the zone of increasing concentrations became more restricted with time until at 96 hours, only the plot well was increasing in Mg concentration. It was also noted that for both Ca and Mg, the 19 hour period in the 22 m well showed a marked decrease and then recovery at the 24 hour period. This would indicate an initial dilution effect at 19 hours from the moving water front reaching this well and diluting the high concentrations of these elements. The neutron probe and well recorder data discussed earlier indicated that the wave front would reach the proximity of the lake at 17 hours. By 19 hours, at the frontal peak, this effect could thus be observed and the chemical data again seemed to confirm the physical flux data.

Sodium

Sodium was the only cation added to the soil system in concentrations greatly in excess of the ambient rain concentrations, the lake water being high in sodium. This is probably the consequence of the long term effect of sea salts in the rain water and evaporation at the lake surface. Natural background concentrations and changes in concentrations were thus difficult to observe in the plot leachates Since the plots were irrigated, the soils, thus soil solutions, were quickly "contaminated" with sodium However, the well data do indicate water table concentration gradients. The concentration of Na in the plot well was the same as the lake in the preirrigation samples. This was the result of thousands of gallons of lake water having been applied to the plot in the acid rain study over the two years. However, there was a slight increasing gradient for Na as we approached the proximity of the lake itself along the water table. The decrease with distance from the plot well could be seen in both the lakeside and inland side of the plot when observing the transect data.

An important observation could be made for the Na data in the near lake wells. The Na data for the lake over the 7 sampling times showed a mean of 3.47 mg/L with a standard deviation of 0.07. The well 4 meters distance from the lake edge showed a Na concentration of 2.02 with a standard deviation of 0.13. If the lake water were draining to the soil water table, we would not expect to have the high Na negative gradient over such a short distance considering the hydraulic conductivity. Thus there must be very limited inland movement horizontally of the lake water. Any movement would thus be in the reverse direction, i.e., towards the lake. The zone of high nutrient concentration could be an evaporation zone which would extend around the lake.

pH

There was a natural increase in pH with depth and this trend was observed throughout the various sampling periods. The means for the soil solutions at 15, 75, 150, and 300 cm depths were 6.86, 6.81, 7.34, and 7.33 pH, respectively. There was a natural increasing pH gradient from the plot well to the 3 wells along the transect However, this natural (i.e , preirrigation) data could have resulted, in the case of the plot well data, from many previous gallons of irrigation with lake water at a pH of 4.6 If the true background pH in the plot well were at the pH of the other wells initially, we would expect a decreasing pH effect at the plot well water table which was already artificially lower. Indeed, the preirrigation pH in the plot well was 5.67, which is intermediate between 6.8 and 4.6. The wells maintained relatively constant pH levels with time. however, the 22 m well showed a constant decrease from 18 hours to 36 hours thence some recovery to former levels. This followed the patterns of several other ions indicating some mobility of H as it decreased the pH along the ion gradient

Aluminum

Aluminum was relatively uniform with depth in the pre- and post-irrigation samples being 45, 28, 68, and 47 μg/L for the 15, 75, 150, and 300 cm depths, respectively. The same range of concentrations were observed in the lake samples. The lake itself had the highest Al concentration of any soil or well solution samples. There was a general increase in Al in the well samples with time postirrigation. The mean concentrations were 28, 39, 45, and 53 μg/L for preirrigation, 1, 4, and 7 days postirrigation, respectively This could indicate perhaps some Al movement to the lake with time

Electrical conductivity

This determination of mean ionic strength for the various ions in solution confirmed the previous observations for the individual elements Results show an increasing concentration of ions with depth in the natural soil solution. As the acid solutions were applied, the EC at the surface depths increased and peaked at 48 hours and then decreased. By 7 days, initial conditions were being reestablished. The means after 7 days for the 16, 75, 150, and 300 cm depths were 117, 83, 103, and 90 dS/cm, respectively, with the preirrigation levels being 67, 65, 145, and 111 dS/cm, respectively. The means over the profile for the preirrigation, 1, 2, 4, and 7 days, were 97, 99, 121, 107, and 102 dS/cm, respectively. The 48 hour period had the highest activity of ions in the system.

There was a gradient of increasing ionic strength, thus ion content, from the plot well to the lake in the horizontal direction. This gradient was maintained throughout the 14 days although the gradient slope changed as the ions moved towards the lake from the irrigation. The minor fluctuation in the general trend was that the plot well was slightly higher than the 6 m well (immediately below the boundary). This could again be the effect of many gallons of irrigation having been applied to the plot well and resulting in an artificially elevated ionic condition. However, the EC data do suggest that there was indeed a frontal concentration that moved with time to the near lake edge region. The EC in the plot well continually increased with time as the plot water continued to drain throughout this period. At 48 hours there was a discernible peak in the EC in the 6 m well. This peak or wave occurred in the 16 m well by 96 hours and also the 22 m well. By 7 days, all outside plot wells were decreasing in EC which continued to 14 days, the last period for data. This was also the case for the well located inland from the plot well. The plot well itself continued to increase slowly in EC over the 14 day period which showed the continuous effect of the large irrigation rain event on the movement of ions into and through the water table. The 96 hour period was the period of greatest mobility in the water table. This indicated a delayed response in the movement of ions vis-à-vis the physical manifestation of the frontal wave. This delayed response corresponded to the movement of the cations, the iodide anion having moved more rapidly. As indicated from the soil profile studies, the cations would also move differentially in the water table with an overall tendency to initially reverse the ion gradient, then a reversion to the normal. This was clearly observed in the pre-irrigation, 24 hour and 7 day data for the 15, 75, 150, and 300 cm depths. The magnitude of the movement of the ions into the water table and along the well transect towards the lake can readily be seen when the average postirrigation data for 14 days for each ion are compared with the preirrigation data for the transect wells (Table 4.10). The Ca, Mg, EC, and especially K and I all showed elevated concentrations postirrigation in the plot, 6 m and 16 m wells compared with the pre-irrigation concentrations. In the more distance wells from the plot well, i.e., the wells nearer the lake, the reverse trend occurs whereby a breakthrough or decreasing of the ion natural gradient was occurring as a result of the dilution effect of the 38 cm irrigation. This was

Table 4 10 Concentration of ions in the transect wells before and after a 3̄6 cm irrigated acid rain.

			Well identification					
			27 m	22 m	16 m	6 m	Plot	
Parameter	Irrigation		Distance from lake (m) 0	5	11	21	27	42
Ca	Pre		1.3	12.5	3.4	1.7	2.7	
	Post	$\bar{x}$*	1.34	12.27	3.85	3.40	3.14	1.76
		S.D.**	.049	.54	.48	1.19	.53	.169
Mg	Pre		.83	1.86	.49	25	.21	
	Post	$\bar{x}$	.82	1.81	.55	.35	.29	.33
		S.D.	.028	111	064	.063	.073	.028
K	Pre		.35	1.02	.79	.88	.56	
	Post	$\bar{x}$	.41	.95	1.24	1.39	69	1.21
		S.D.	039	.16	1.11	.60	.12	.64
Na	Pre		3.4	2.2	2.3	1.7	3.3	
	Post	$\bar{x}$	3.47	2.04	2.21	1.86	3.16	2.63
		S.D.	.069	14	.083	.72	.219	.025
pH	Pre		4.65	7.57	6.41	6.21	5.67	
	Post	$\bar{x}$	4.66	6.31	6.11	6.11	5.73	5.56
		S.D.	.015	.260	.405	.251	.269	.093
EC (dS/cm)	Pre		43	114	58	35	39	
	Post	$\bar{x}$	43.7	108.7	55.1	37.4	44.7	27.3
		S.D.	1.26	5.59	3.27	3.88	5.65	2.62
I	Pre		.017	.128	.12	.018	.014	
	Post	$\bar{x}$	.031	.069	.040	.035	.037	.020
		S.D.	.033	051	.035	.018	.034	.013
Al	Pre		90	30	40	95	10	
	Post	$\bar{x}$	88	43	47	88	17	17
		S.D.	7.5	6.9	11.4	12.4	8.8	4.7

*mean

**standard deviation

seen for EC, Ca, Mg, K, and I. Except for I which had moved more rapidly through the system, it would appear that the cations moved to a distance between the 16 and 22 m wells or a horizontal distance from the plot boundary of from 12 to 18 meters in the 14 days for a rate of approximately I m/day

Ion Mobility--Losses and Adsorption

Ion Net Losses

In order to assess the magnitude of the effects of the acid rain (H, NO_3-N, and SO_4) treatments, the background or control losses must be set at zero, i.e., subtracted from the treatments 3.0 and 3.7 pH. Then the estimates of ion net losses can be made past the two depths of 15 and 75 cm.

Although the ambient rain natural to the site was lower in ion concentrations than that added in the simulated acid rain, there was a close agreement in the chemistry of simulated rain to canopy throughfall In a forested system, the throughfall chemistry from a closed canopy has greater implication than that of the ambient rain (Tables 2.2, 4.11).

Field experiment, comparison within element

Comparing the analytical data of the leachates at 15 and 75 cm depth in the plots with the simulated control rain provides information on ion movement under natural conditions (Table 4.12).

Table 4.11. Ion input to the soil from various sources at the field site

	McCloud Lake[1]		Ambient Rain[2]		Throughfall[3]	
Parameter	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
Ca	1.29	.064	0.40	.020	1.30	.066
Mg	0.82	.067	0.12	.010	0.38	.031
K	0.64	.016	0.20	.005	6.31	.162
Na	3.12	.136	0.44	.019	0.39	.017
NH_4-N	0.20	.014	0.10	.007	0.46	.032
NO_3-N	0.044	.003	0.19	.014	0.46	.033
H	0.022	.022	0.029	.029	0.025	.025
SO_4	7.3	.152	2.2	.046	10.7	.223
PO_4-P	0.003	--	0.002	--	0.09	--
Cl	5.5	.155	1.01	.028	1.56	.044
EC (dS/cm)	43	.559	10	13	--	--

[1] lake water used in simulated acid rain

[2] Gainesville

[3] mean for mixed forest canopy

Table 4.12 Loss of ions from 15 and 75 cm depths in field plots after 100 cm irrigated acid rain at 4.65 pH.

Parameter	Depth				Ion input in irrigated acid rain	
	15 cm		75 cm			
	kg/ha	Ex10^3/ha*	kg/ha	Ex10^3/ha	kg/ha	Ex10^3/ha
Ca	35.2	1.76	36.4	1.82	13.0	0.65
Mg	7.8	0.64	7.7	0.63	8.3	0.68
K	16.7	0.43	17.7	0.45	6.5	0.17
Na	39.4	1.71	38.2	1.66	31.5	1.37
Al	0.46	0.05	0.30	0.03	0.90	0.10
H	0.01	0.01	0.01	0.01	0.22	0.22
NH_4-N	4.1	0.29	7.6	0.54	2.0	0.14
SO_4	72	1.50	44	0.92	73.6	1.53
NO_3-N	2.2	0.16	4.5	0.32	0.44	0.03
Cl	62.6	1.76	55.5	1.56	55.5	1.56
P	.011	--	0.009	--	0.003	--

*E x 10^3/ha = equivalents x 10^3/hectare or kiloequivalents/hectare

The control data show that there was a uniform loss of elements (kg/ha) past both 15 and 75 cm for Ca, Mg, K, Na, N, Cl, and P. For Al, SO_4, NH_4-N, and NO_3-N, this was not the case. For Mg, Na, and Cl, the loss past the two depths approximated the input in the irrigation rain. For SO_4 and Al, the losses past the 15 cm equalled the input, but at 75 cm, the loss was much less, indicating adsorption or immobilization of these elements with depth. For K and Ca, the loss past the two depths, though uniform, were well above the input concentrations. For NH_4-N and NO_3-N, the losses increased with depth, and at both depths, the losses were greater than the input concentrations. This indicated microbial activity causing a natural production of NO_3-N and NH_4-N near the surface and subsequent movement of these two ions to depth. Aluminum data showed adsorption with depth but losses at both depths were still lower than the ion input concentrations, meaning that there was adsorption in the 0 to 75 cm profile. For H, the input concentration was more than 20 times the losses past the two depths indicating almost total adsorption of this ion.

Calcium. Calcium net loss was greatest for all the cations (Table 4.13). The 3.0 pH treatment showed the greatest loss at the 15 cm depth (49 kg/ha) with 75 cm depth showing a loss of 20 kg/ha. This indicated a reducing loss with depth and a desorption at the 15 cm depth with a readsorption of 60 percent of that amount by 75 cm. The 3.7 pH treatment showed a uniform movement of Ca with depth at lower levels of loss (11 and 12 kg/ha, respectively).

Magnesium. The 3.0 pH treatment showed a decreasing loss of Mg with depth (10 and 7.5 kg/ha) indicating some adsorption. The same trend

Table 4.13. Loss of ions from 15 and 75 cm depths in field plots after 100 cm irrigated acid rain for three treatments

Parameter	Trt. pH	Loss of Ions Acid Rain Treatment Depth (cm) 15	 75	 Treatment minusControl* 15	 75	 Acid Rain Treatment 15	 75	 Treatment minusControl* 15	 75
		kg/ha				(x 10^3/ha			
Ca	3.0	86.4	56.0	49.3	19.6	4.21	2.80	2.46	0.98
	3.7	46.0	48.1	10.8	11.7	2.30	2.42	0.54	0.59
	4.6	35.2	36.4	0	0	1.76	1.82	0	0
Mg	3.0	18.1	15.2	10.3	7.5	1.49	1.25	0.85	0.62
	3.7	10.3	9.3	2.5	1.6	0.85	0.77	0.21	0.13
	4.6	7.8	7.7	0	0	0.64	0.63	0	0
K	3.0	16.7	15.2	0	-2.5	0.43	0.39	0	-0.06
	3.7	15.3	15.0	-1.4	-2.7	0.39	0.38	0	-0.06
	4.6	16.7	17.7	0	0	0.43	0.45	0	0
Na	3.0	42.6	41.1	3.2	2.9	1.85	1.79	0.14	0.13
	3.7	40.3	38.9	0.9	0.7	1.75	1.69	0.04	0.03
	4.6	39.4	38.2	0	0	1.71	1.66	0	0
Al	3.0	14.01	0.44	13.5	0.14	1.56	0.05	1.50	0.02
	3.7	1.13	0.44	0.67	0.14	0.13	0.05	0.07	0.02
	4.6	0.46	0.30	0	0	0.05	0.03	0	0
H	3.0	0.09	0.03	0.08	0.02	0.09	0.03	0.08	0.02
	3.7	0.02	0.02	0.01	0.01	0.02	0.02	0.01	0.01
	4.6	0.01	0.01	0	0	0.01	0.01	0	0
NH_4-N	3.0	6.3	4.7	2.2	-2.9	0.45	0.34	0.16	-0.21
	3.7	4.3	3.5	0.2	-4.1	0.31	0.25	0.02	-0.19
	4.6	4.1	7.6	0	0	0.29	0.54	0	0
SO_4	3.0	326	145	254	101	6.79	3.02	5.29	2.10
	3.7	115	84	43	40	2.40	1.75	0.90	0.83
	4.6	72	44	0	0	1.50	0.92	0	0
NO_3-N	3.0	7.8	7.2	5.6	2.7	0.56	0.51	0.40	0.19
	3.7	2.6	4.4	0.4	0	0.19	0.31	0.03	0
	4.6	2.2	4.5	0	0	0.16	0.32	0	0
Cl	3.0	70.7	77.8	8.1	22.3	2.00	2.19	0.24	0.63
	3.7	63.6	60.6	1.0	5.1	1.79	1.71	0.03	0.15
	4.6	62.6	55.5	0	0	1.76	1.56	0	0
F	3.0	.011	.010	0	0				
	3.7	.008	.010	0	0				
	4.6	.011	.009	0	0				

* Control is the 4.6 pH treatment

occurred for the 3.7 treatment (2.5 and 2 kg/ha). The magnitude of the magnesium loss was greater for the 3.0 than the 3.7 pH treatments at both depths.

Potassium. Potassium loss was very uniform with treatment and depth. The 75 cm depth, in fact, showed potassium losses less than the control for both treatments indicating a depletion.

Sodium. The same trend followed for sodium as for potassium. There was, however, some loss of sodium from the 15 cm depth indicating some displacement.

Aluminum. Aluminum showed the greatest percentage differential depth loss of all the elements at 3.0 treatment (13.6 vs 0.14 kg/ha). Thus 97 percent of the soluble Al at 15 cm was immobilized by 75 cm depth. The 3.7 treatment was much lower in magnitude of loss (0.7 vs 0.14 mg/L, respectively) for 15 and 75 cm. At 75 cm, there was a uniform loss of Al regardless of treatment being 0.14 kg/ha. Thus much less Al was removed by the 3.7 pH than by the 3.0 pH treatment.

Hydrogen. The greatest net loss of H was with the 3.0 pH treatment at 15 cm depth. All other losses of H were very low. This indicated the great exchange ability of H as it acted in its important role in exchange reactions. Thus treatment had little effect at the lower pH and lower depth in the Candler sand.

Ammonium-H. There was an elevated loss (2.2 kg/ha) of NH_4-N from the 3.0 pH treatment at 15 cm. There was little loss from 3.7 pH. This indicated microbial conversion however, in both cases, since the control itself was two times the concentration of the input NH_4-H. The control data showed that HH_4-H accumulated naturally at depth, yet the treatments showed decreased concentrations with depth. This could have been due to exchange by other elevated cations and removal of the NH_4-N to below 75 cm

Sulfate. Sulfate, the major anion in the rain, was detected in large quantities moving past both 15 and 75 cm for both treatments. The 3.0 pH treatment showed the greatest net loss as would be expected, the differential loss being also large, indicating adsorption of SO_4 in the 15 to 75 cm depth. When compared with the amount added (420 kg/ha), 60% and 24% were lost past for 15 and 75 cm depth, respectively. For 3.7 treatment, there was uniform loss past 15 and 75 cm being 43 and 40 kg/ha, respectively, or 31 and 29%, respectively, of the input SO_4.

Nitrate-N. For the 3.0 pH treatment, there was a 50% reduction in the NO_3-N concentration between these two depths. In addition, these concentrations, being 5.6 and 2.7 kg/ha, respectively, were much below the input concentration of 20.4 kg/ha. The magnitude of the reduction could be clearly seen, having been the result of absorption by plant roots, leaching to depth, and conversion and adsorption by soil microorganisms. For the 3.7 pH treatment, there was little net NO_3-N detected moving past these two depths indicating little residual effect of this acid treatment when compared to the control. When considering that 5.0 kg/ha of NO_3-N was added in the rain, very little of it passed the 75 cm depth. Thus at 15 cm, 73% and 98% of the input NO_3-N for 3.0 and 3.7 pH treatments, respectively, were absorbed or converted. The figures for 75 cm were 85% and 100%, respectively.

Chloride. Chloride, like sodium, was greatly elevated in the simulated acid rain compared with the ambient rain. The mobility of this element could readily be seen in the rather uniform movement with treatment and depth. Elevated quantities of chloride were detected at the 15 cm depths for all treatments when compared with the added quantities in the simulated acid rain. This could be the result of residual chloride in the surface depths from interim irrigation conditions and also amounts of chloride from the ambient interirrigation rain events.

Phosphorus. Very low quantities of phosphorus were detected in the 15 and 75 cm depths. Nonetheless, it can be seen that, although there was little difference with treatment, there was slightly more P in the 15 than the 75 cm depth. This was the effect of desorption of P from the soil surface.

Total quantities removed of the 11 parameters from the 15 cm layer for the three treatments 3.0, 3.7, and 4.6 pH were 584, 301, and 241 kg/ha, respectively. Those for the 75 cm depths were 360, 366, and 218 kg/ha, respectively. These figures represent a 25 percent reduction (conversion or adsorption) of these elements as they moved from the 15 to 75 cm depth. Net losses for 3.0 pH for 15 and 75 cm were 343 and 142 kg/ha, respectively. Net losses for 3.7 pH for these two depths were 60 and 48 kg/ha, respectively. Thus loss past 15 cm was 5.7 times greater for 3.0 pH than 3.7 pH. This ratio was reduced to 3.0 times by 75 cm depth.

Column experiment, comparison within element

The laboratory column experiment was conducted to give a comparison of data from a laboratory technique compared with the field experimental data. Both experiments had 100 cm simulated acid rain. However, unlike the field experiment where the acid rain was imposed in 17 rain events under unsaturated conditions, the laboratory experiment imposed the 100 cm total rain as one event under saturated conditions at a fairly high rate of application under constant pressure using a peristaltic pump. Thus there were fundamental differences. However, for a laboratory experiment to be of practical value in assessing a large number of soils for the effect of acid rain and simulating natural conditions, the method must be relatively simple, reproducible, and rapid

The data showed that there was not a uniform loss of elements (kg/ha) past the 15 and 75 cm depths for the control except for nitrate which was in relatively low concentration in the acid rain. At 15 cm, only Na and NO_3-N approximated the input concentrations and only NO_3-N at the 75 cm depth. Adsorption with depth was indicated for Mg, K, Al, H, and SO_4. A desorption or increase in 75 cm over 15 cm depth was noted for Ca and Cl. The data for net losses (treatment minus control) showed that there was a net loss (kg/ha) for all elements for both 15 and 75 cm depths (Table 4.14).

Upon setting the control data at zero, and thus nullifying differential adsorption and desorption phenomena with depth and among ions, there was an overall net loss of each ion at each of the 15 and 75 cm depths for the treatments 3.7 and 3.0 pH (Table 4.15).

Calcium. There was a uniform loss of Ca from the 15 and 75 cm depth for the 3.7 pH treatment indicating uniform displacement with depth (10 and 9 kg/ha, respectively). However, for the 3.0 treatment, more Ca was lost past the 75 cm depth than past the 15 cm depth, indicating greater

Table 4.14 Loss of ions from 15 and 75 cm soil columns after 100 cm applied acid rain at 4.65 pH

Parameter	Depth				Ion input in irrigated acid rain	
	15 cm		75 cm			
	kg/ha	Ex10^3/ha	kg/ha	Ex10^3/ha	kg/ha	Ex10^3/ha
Ca	7.2	0.36	18.3	0.91	13.0	0.65
Mg	7.1	0.58	4.2	0.35	8.3	0.69
K	7.8	0.20	4.2	0.11	6.5	0.17
Na	30.5	1.33	28.3	1.23	31.5	1.37
Al	3.0	0.33	1.7	0.19	0.9	0.10
H	0.14	0.14	0.08	0.08	0.22	0.22
SO$_4$	56	1.17	48	1.00	73.7	1.53
NO$_3$-N	0.5	0.04	0.4	0.03	0.44	0.03
Cl	69.4	1.96	80.7	2.27	55.5	1.56

Table 4.15. Loss of ions from 15 and 75 cm soil column after 100 cm applied acid rain for three treatments.

		Loss of Ions							
		Acid Rain Treatment		Treatment minus Control*		Acid Rain Treatment		Treatment minus Control*	
		Depth							
Parameter	Tmt. pH	15 cm	75 cm	15 cm	75 cm	15 cm	75 cm	15 cm	75 cm
Ca	3.0	43.6	69.4	34.4	51.1	2.18	3.46	1.83	2.55
	3.7	17.6	27.5	10.4	9.2	0.88	1.37	0.52	0.46
	4.6	7.2	18.3	0	0	0.36	0.91	0	0
Mg	3.0	14.6	13.6	7.5	8.8	1.20	1.13	0.82	0.72
	3.7	11.8	9.2	4.7	5.0	0.97	0.76	0.39	0.41
	4.6	7.1	4.2	0	0	0.58	0.35	0	0
K	3.0	8.0	6.1	0.2	1.9	0.21	0.16	0.01	0.05
	3.7	7.9	5.6	0.1	1.2	0.20	0.14	0	0.03
	4.6	7.8	4.2	0	0	0.20	0.11	0	0
Na	3.0	33.0	33.5	2.5	5.2	1.43	1.46	0.10	0.23
	3.7	32.9	30.9	2.4	1.6	1.43	1.34	0.10	0.11
	4.6	30.5	28.3	0	0	1.33	1.23	0	0
Al	3.0	57.9	26.3	54.9	24.6	6.43	2.92	6.10	2.73
	3.7	13.4	2.5	10.1	0.8	1.49	0.28	1.16	0.09
	4.6	3.0	1.7	0	0	0.33	0.19	0	0
H	3.0	0.80	0.45	0.66	0.37	0.80	0.45	0.66	0.37
	3.7	0.30	0.12	0.16	0.04	0.30	0.12	0.16	0.04
	4.6	0.14	0.08	0	0	0.14	0.08	0	0
SO_4	3.0	394	224	338	176	8.21	4.67	7.04	3.68
	3.7	119	84	81	36	1.47	1.75	0.69	0.75
	4.6	56	48	0	0	1.17	1.00	0	0
NO_3-N	3.0	18.7	21.1	18.2	20.7	1.34	1.51	1.28	1.48
	3.7	2.0	4.7	1.5	4.3	0.14	0.34	0.20	0.31
	4.6	0.5	0.4	0	0	0.06	0.03	0	0
Cl	3.0	84.0	123.1	15.3	42.4	2.39	3.41	0.43	1.14
	3.7	91.8	101.2	22.2	21.0	2.58	2.85	0.62	1.58
	4.6	69.6	80.7	0	0	1.96	2.27	0	0

* Control is the 4.6 pH treatment

displacement with depth under more acid conditions of this element. The loss by the 3.0 treatment was 3.5 times that for the 3.7 treatment at 15 cm and 5.6 times at 75 cm depth.

Magnesium. For the 3.7 pH, there was slightly more loss past the 75 than the 15 cm depth (5.0 and 4.7, respectively) indicating a desorption process. Magnesium loss by the 3.0 pH treatment was approximately 1.7 times that lost by the 3.7 treatment for both depths, showing a uniform loss of Mg with depth for both treatments.

Potassium. There was little net loss of K past the 15 cm depth for either of the treatment 3.7 and 3.0 pH. However, there was increased loss past the 75 cm depth and uniformly so with treatment. The loss was small being only 1.3 times that for the control on average. Thus, although there was greater net loss of K with depth, the loss was relatively small.

Sodium. There was approximately a uniform loss of Na in the 15 cm depth over treatment. There was a proportionally larger loss past the 75 cm depth for the 3.0 treatment, indicating a displacement of the sodium in the soil at depth by the most acid treatment, 3.0 pH.

Aluminum. Large net amounts of Al moved past the 15 cm depth for both treatments 3.0 and 3.7 pH, being 55 and 10 kg/ha, respectively. There was a much lower loss past the 75 cm depth for these two treatments, being 25 and 1 kg/ha, respectively. This suggested readsorption or precipitation of the displaced Al with depth, the adsorption for 3.0 and 3.7 being 55% and 92%, respectively.

Hydrogen. The same trend occurred for H as for Al, except that the magnitude of loss and readsorption with treatment was much less

Adsorption with depth was 44% for 3.0 pH and 75% for 3.7 pH, respectively.

Sulfate. Sulfate, the major added ion in the acid rain, was dominant in the soil solution as it passed both the 15 and 75 cm soil depth. The net quantity of sulfate passing the 15 cm depth was greater than that passing the 75 cm depth indicating net adsorption with depth for all treatments. When comparing the two treatments, 3.0 and 3.7 pH, the largest quantity of sulfate passed the 15 cm at 3.0 treatment and the lowest quantity of sulfate passed the 75 cm at the 3.7 treatment. Adsorption at 75 cm compared to 15 cm was 51% for 3.0 pH and 56% for 3.7 pH.

Nitrate-N. Nitrate-N was the second major anion added in the system and net quantities were greater at the 75 cm depth for both treatments. This was a reversal of the trend for SO_4 and indicated gross movement with depth, as well as natural additions from other sources.

Chloride. Both treatments 3.0 and 3.7 pH showed net losses at both depths of 15 and 75 cm. The 3.0 treatment had the highest loss of chloride at both depths. The 75 cm depth showed greater net loss than the 15 cm depth. This indicated that there was a treatment effect of removing chloride slowly and constantly from the soil, greater quantities being removed from greater depths due to much more soil volume which contributed to the chloride loss.

Total quantities removed of the 9 major parameters from the 15 cm layer for the three treatments 3.0, 3.7, and 4.6 pH were 657, 307, and 182 kg/ha, respectively. Those for the 75 cm depth were 520, 298, and 194 kg/ha, respectively. Net losses at 15 cm for 3.0 and 3.7 pH treatment were 475 and 125 kg/ha, respectively. At 75 cm, the net losses were 326 and 105 kg/ha, respectively. The lower the pH treatment and the closer to the surface, the greater the net loss of ions.

Field experiment, comparison among elements

In order to assess the relative losses of the major nutrient ions plus H and Al ions from the field and column soil systems, a conversion to the equivalent basis must be made from kg/ha to equivalents per hectare (E x 10^3/ha).

15 cm, pH 3.0 treatment. Among the cations, Ca was lost in greatest quantities with K showing very low net losses. Among the anions, SO_4 was by far the element of greatest net loss from the system, also being the major added ion. Phosphorus was least affected by the treatments. The orders of decreasing net losses were

Element	Ca	Al	Mg	H	K	SO_4	NO_3-N	P
E x 10^3/ha	2.46	1.50	0.85	0.08	0	5.29	0.40	0.01
kg/ha	49.2	13.5	10.3	0.08	0	254	5.8	0

15 cm, pH 3.7 treatment. The greatest net loss was with Ca. Potassium showed the lowest net loss for the cations. For the anions, SO_4 showed the greatest net loss. The orders of decreasing net losses were

Element	Ca	Mg	Al	H	K	SO_4	NO_3-N	P
E x 10^3/ha	0.54	0.21	0.07	0.01	0	0.90	0.03	0
kg/ha	10.8	2.6	0.67	0.01	0	43	0.4	0

75 cm, pH 3.0 treatment. Among the cations, Ca was again lost in greatest net quantities. For the anions, SO_4 was lost in greatest net quantity.

Element	Ca	Mg	Al	H	K	SO_4	NO_3-N	PO_4-P
E x 10^3/ha	0.90	0.62	0.02	0.02	0	2.10	0.19	0
kg/ha	19.6	7.5	0.14	0.01	0	101	2.7	0

75 cm, pH 3.7 treatment. Calcium and SO_4 were again the ions of greatest net losses

Element	Ca	Mg	Al	H	K	SO_4	NO_3-N	PO_4-P
E x 10^3/ha	0.59	0.13	0.02	0.01	0	0.83	0	0
kg/ha	11.7	1.6	0.14	0.01	0	40	0	0

Column experiment, comparison among elements

15 cm, 3.0 treatment. Among the cations, Al was lost in greatest net quantity, with K showing little net loss

Element	Al	Ca	H	Mg	K	SO_4	NO_3-N
E x 10^3/ha	6.10	1.83	0.66	0.62	0.01	7.04	1.30
kg/ha	54.9	36.4	0.66	7.5	0.2	33.8	18.2

15 cm, 3.7 treatment. Aluminum was again the cation of greatest net loss with SO_4 the anion of greatest net loss.

Element	Al	Ca	Mg	H	K	SO_4	NO_3-N
E x 10^3/ha	1.16	0.52	0.39	0.16	0.01	1.69	0.43
kg/ha	10.1	10.4	4.7	0.16	0.1	81	1.5

75 cm, 3.0 treatment. Even at 75 cm, Al loss was slightly more than Ca and was the cation of greatest net loss. Sulfate was the anion of greatest net loss

Element	Al	Ca	Mg	H	K	SO_4	NO_3-N
E x 10^3/ha	2.73	2.55	0.72	0.37	0.05	3.48	1.48
kg/ha	24.6	51.1	8.8	0.37	1.9	167	20.7

75 cm, 3.7 treatment. Calcium showed the greatest net loss for the cations with SO_4 for the anions.

Element	Ca	Mg	Al	H	K	SO_4	NO_3-N
E x 10^3/ha	0.46	0.41	0.09	0.04	0.03	0.58	0.31
kg/ha	9.2	5.0	0.8	0.04	1.2	36	4.3

Cation loss compared to the CEC

The distribution of the Ca, Mg, K, and Na on the exchange sites expressed as kg/ha was 43.9, 14.8, 18.2, and 5.9, respectively (Table 4.16) for a total of 82.8 kg/ha. When converted to an equivalent basis (E x 10^3/ha), the cation distribution was 2.19, 1.22, 0.47, and 0.26, respectively, for a total of 4.14 E x 10^3/ha. The distribution was 53, 30, 11, and 6 percent for Ca, Mg, K, and Na, respectively, of the base exchange complex. Since the total CEC was 87.2 E x 10^3/ha, these four cations occupied 4.7 percent of the CEC.

Cation loss--calcium. Of the three major plant growth cations in the system, Ca showed the greatest variation in loss for the three treatments (Table 4.17). For the 15 cm depth, the 3.0 treatment removed 77 percent of the Ca on the exchange sites, while the 3.7 treatment removed 32 percent, and the 4.6 treatment (control) removed only 13 percent. These corresponded to 1.69, 0.70, and 0.28 E x 10^3/ha, respectively. For the 75 cm depth, the order of decreasing loss remained the same, but the magnitude was greater.

Cation loss--magnesium. Magnesium was the second major cation most readily lost from the soil. For the 15 cm depth, the removal for the treatments 3.0, 3.7, and control were 63, 51, and 30 percent, respectively. These corresponded to 0.77, 0.62, and 0.37 E x 10^3/ha, respectively. The range was relatively narrow. For the 75 cm depth, there was a lower loss compared with the 15 cm depth.

Table 4.16. Distribution of cations on the exchange sites at 0 to 15 cm depth

Element	kg/ha	E x 10^3/ha	Percent of base saturation
Ca	43.9	2.19	52.9
Mg	14.8	1.22	29.5
K	18.2	0.47	11.4
Na	5.9	0.26	6.2
Total	82.8	4.14	100

Table 4 17 Reduction in the base saturation after 100 cm acid rain for three treatments at two soil depths

Depth (cm)	Element	Treatment	Cation Loss		Reduction in Base Saturation		
			Kg/ha	Kmol^{3}/ha	%	Kg/ha	Kmol^{3}/ha
10	Ca	NH_4OAC	43.9	2.19			
		Rain + NH_4OAC	56.9	2.84	100		
		3.0	43.6	2.18	77	13.8	1.08
		3.7	17.6	0.91	32	14.0	0.70
		4.8	7.2	0.38	13	5.7	0.28
		Rain	13.0	0.65			
	Mg	NH_4OAC	14.8	1.22			
		Rain + NH_4OAC	22.3	1.88	100		
		3.0	14.6	1.20	63	9.32	0.77
		3.7	11.8	0.97	51	7.55	0.62
		4.6	7.1	0.58	30	4.44	0.37
		Rain	8.3	0.69			
	K	NH_4OAC	18.2	0.47			
		Rain + NH_4OAC	24.7	0.63	100		
		3.0	8.0	0.21	32	6.37	0.16
		3.7	7.9	0.20	32	6.12	0.15
		4.8	7.8	0.20	32	6.12	0.15
		Rain	6.3	0.16			
	Ca+Mg+K	NH_4OAC	76.9	3.86			
	Ca+Mg+K+Na	NH_4OAC	88.8	4.14			
		Rain+NH_4OAC	104.7	5.33	100		
		3.0	66.2	3.39	63	48.5	2.42
		3.7	37.3	2.08	36	27.6	1.39
		4.8	22.1	1.16	21	16.3	0.81
		Rain	27.8	1.45			
75	Ca+Mg+K	NH_4OAC	210.9	11.21			
	Ca+Mg+K+Na	NH_4OAC	224.8	11.96			
		Rain+NH_4OAC	238.7	12.7	100		
		3.0	89.1	4.75	37	78.0	4.15
		3.7	42.3	2.27	18	38.0	2.02
		4.6	26.7	1.37	11	23.2	1.23
		Rain	27.8	1.48			

Cation loss--potassium. Potassium showed the smallest variation in loss over treatment and the smallest magnitude of loss of the three major plant nutrients as cations. For the 15 cm depth, for 3.0, 3.7, and control, the percentage loss was 35, 34, and 34, respectively. The corresponding equivalence figures were 0.16, 0.15, and 0.15 E x 10^3/ha, respectively. For the 75 cm depth, there was a lower loss of K and a slight widening of the loss with treatment.

Total loss of Ca, Mg, and K from the base saturation. The total loss at 15 cm of the three cations for treatments 3.0, 3.7, and control were 63, 36, and 21 percent, respectively, of the total amount present initially for these three cations. When considering that Na also included 6.2 percent of the base saturation, then the loss of these three cations Ca, Mg, and K, for the three treatments 3.0, 3.7, and control, constituted 59, 34, and 20 percent of the base saturation at the 15 cm depth. These losses converted to 49, 28, and 15 kg/ha or 2.42, 1.37, and 0.81 E x 10^3/ha. Since the distribution of the cations on the exchange complex at 75 cm were at the same initial percentages, the percentage losses for 3.0, 3.7, and control were 39, 19, and 11 percent, respectively, of the base saturation. Thus the cation losses from 75 cm were a lower percentage of the total base saturation than the losses from the 15 cm depth.

Total loss of Ca, Mg, and K from the total exchange. The total CEC of this soil for 15 cm depth was 3.41 me/100 g or 87.2 E x 10^3/ha (Table 4.18). This corresponded to about 1744 kg/ha for Ca, Mg, K, Na, H, and Al. Since the total cation loss for 3.0, 3.7, and control treatments was 2.42, 1.39, and 0.81 E x 10^3/ha, respectively, the net change

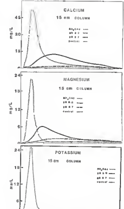


Figure 4.15. Comparison of exchangeable cations with cation loss for three acid rain treatments in 15 cm soil columns.

Table 4 18 Loss of Ca, Mg, and K from the cation exchange complex at two soil depths

Depth cm	Cation exchange capacity E x 10^3/ha	Acid rain tmt pH	Cation loss E x 10^3/ha	% of CEC
15	87.2	3.0	2.42	2.78
		3.7	1.39	1.59
		4.6	0.81	0.91
75	271.2	3.0	4.15	1.53
		3.7	2.02	0.70
		4.6	1.23	0.20

if the CEC remained static would be a 2.8, 1.6, and 0.9 percent reduction in the base saturation. For the 75 cm depth, the three treatments would reduce the base saturation by only about 50 percent of these amounts.

Depletion of exchangeable cations in the soil by acid treatment

Soil samples were taken in February and August and represented the pre- and postsamples of the acid rain treatments in the field experiment.

The preirrigation samples showed uniform quantities of exchangeable cations (Ca, Mg, K) on the exchange sites (Table 4.19). For the three transects of three plots each, the total cations equalled 2.53, 2.53, and 2.51 E x 10^3/ha for the 15 cm depth for control, 3.7, and 3.0 pH, respectively. For the 15 to 75 cm depth, the corresponding quantities of ions on the exchange sites were 3.73, 3.69, and 3.87 E x 10^3/ha. This showed uniformity in cation balance among plot soils. After the 100 cm of acid rain treatments were imposed on the soil, the quantities of cations on the exchange sites at the 15 cm depth, for the control, pH 3.7, and pH 3.0 were 3.50, 2.69, and 1.84 E x 10^3/ha, respectively. This clearly showed a decrease in exchangeable cations in the soil with decreased pH of the treatments. However, there was the reverse trend of increased loss of cations in the soil leachate (removed in the 17 acid rain treatments imposed during March-July period) with decreasing treatment pH. The losses for control, pH 3.7, and pH 3.0 were 2.83, 3.50, and 6.13 E x 10^3/ha, respectively.

If there were only exchangeable cations and not any additional losses of cations (for example, by weathering processes), the loss of cations from the soil exchange sites should closely approximate the loss via the soil leachate. For the 3.7 treatment at the 15 cm depth, the

Table 4.19 Depletion of exchangeable cations by three acid rain treatments

Depth (cm)	Treatment	Preirrigation soil				Irrigation leachate		Postirrigation soil				
		Extraction by NH_4OAc				Acid rain		Extraction by NH_4OAc				
		Ca	Mg	K	Total	Total	Net*	Ca	Mg	K	Total	Net
		E x 10^3/ha										
0-15	4.6	1.54	0.51	0.48	2.53	2.83		2.08	0.79	0.63	3.50	
	3.7	1.54	0.51	0.48	2.53	3.50	+0.67	1.47	0.59	0.63	2.69	-0.81
	3.0	1.54	0.51	0.48	2.51	6.13	+3.30	0.88	0.33	0.63	1.84	-1.66
15-75	4.6	1.87	0.84	1.02	3.73	2.90		1.38	1.56	2.04	4.98	
	3.7	1.59	0.89	1.11	3.69	3.56	+0.66	1.95	1.82	2.18	5.96	+0.98
	3.0	1.60	1.11	1.11	3.87	4.46	+1.56	2.18	1.38	2.00	5.56	+0.58

*Net = tmt - control (4.6 pH)

net loss in the soil was 0.61 E x 10^3/ha. The soil leachate loss was 0.87 E x 10^3/ha. This would indicate mostly exchangeable losses. For the 3.0 treatment, the loss from the soil was 1.99 E x 10^3/ha, but the loss in the soil leachate was 3.30 E x 10^3/ha. There were obviously cation losses over time above those from the immediate exchange sites. These were not additional input cations under from natural sources such as the rain since these figures are net (treatment minus control) results. Thus the cation loss of 1.66 E x 10^3/ha in the soil was a reflection of only 60 percent of the actual loss over time under natural conditions, and is an indication of the replenishing cation capacity of the soil which countered the depleting effects of the 3.0 pH treatment. The leachate loss was thus a truer indicator of cation loss than was the soil decrease in exchangeable cations. The former was the sum of many short-term irrigation pulses, whereas the latter was a post-experiment determination which allowed for the long-term interpulse establishment of cation equilibrium conditions.

For the 75 cm depth, there were increased losses of 0.99 and 1.56 x E x 10^3/ha in the soil leachates for 3.7 and 3.0 pH treatments, respectively. However, the postirrigation soil samples also showed increased cation concentrations, not corresponding losses as with the 15 cm depth. These increases were 0.99 and 0.58 E x 10^3/ha, respectively. This indicated adsorption of removed cations from the 0-15 cm depth which masked any tendency for a decrease in soil cations due to removal by H^+ in this 15-75 cm soil region. The overall effect was an increase of 0.32 E x 10^3/ha in the 15-75 cm depth resulting from the 3.7 treatment. Thus, the 100 cm of 3.7 pH acid rain removed cations to below the

75 cm depth, but also increased the available cation supply in the soil in the 15-75 cm depth, i.e., increased the base saturation. For the 3.0 treatment, despite the countering readsorption effects, there was a net loss of cations in the soil from the 15-75 cm depth of 0.98 E x 10^3/ha. The 100 cm of 3.0 pH acid rain removed below 75 cm three times the amount of cations as the 3.7 pH treatment and increased the base saturation only half as much. Thus both treatments were clearly moving cations into the 15-75 cm depth range and removing 50 percent of the 3.0 pH treatment ions and 100 percent of the 3.7 pH treatment ions below 75 cm and out of the range of both shallow and deep rooted plants.

Decrease in soil pH by acid treatment. The preirrigation soil pHs for the three treatment transects (averaged over the three plots per transect) in the field were very similar on the horizontal plane for each depth. However, on the vertical plane, there was a natural decrease with depth.

For the 0-15 cm depth, the preirrigation pHs for the soils in the three treatment transects 4.6 (control), 3.7, and 3.0 pH were 4.83, 4.87, and 4.83 pH, respectively, for an average of 4.84. Corresponding figures for the 15-75 cm depth were 4.53, 4.57, and 4.69 pH, respectively, for an average of 4.60 pH. The decrease with depth from 0-15 to 15-75 cm was 0.24 pH units.

The postirrigation soil pHs for the three transects did show a slight decrease in pH with increasing acid treatment for both depths. For the 0-15 cm depth, the postirrigation soil pHs for the treatments 4.6, 3.7, and 3.0 pH were 5.0, 4.83, and 4.63 pH, respectively. Corresponding figures for the 15-75 cm depth were 4.73, 4.63, and 4.53 pH, respectively.

Thus, based on the control, the 3.7 pH treatment decreased the soil pH in the 0-15 and 15-75 cm depths by 0.2 and 0.1 pH units, respectively. The 3.0 pH treatment decreased the soil pH in the 0-15 and 15-75 cm depth by 0.4 and 0.2 pH units, respectively. Thus both treatments reduced the soil pH, the 3.0 pH treatment having the greater effect. There was noted a natural rise in soil pH over the irrigation period, probably due to seasonal fluctuation.

Mass Balance and Ion Losses with Depth

When the data in kg/ha are converted to E x 10^3/ha, the mass balance can be readily assessed. Table 4.20 shows the mass balance figures for the column experiment for the three treatments the corresponding data for the field experiment. Included in the cation balance were Ca, Mg, K, Na, Al, and H. Included in the anion balance were SO_4, NO_3-N, P, and Cl. The percent difference for cation anion losses compared to the total loss was 3.5 percent for the column experiment and 12.2 for the field experiment.

Column experiment (Table 4.20)

For the control, there was a uniform movement of total ions past both 15 and 75 cm depth (6.11 and 6.17 E x 10^3/ha, respectively). Although the individual ions moved differentially in response to the 4.65 pH (control) treatment past these two depths, an overall balance was maintained and an overall adsorption trend was not detected.

For the pH 3.7 treatment, there was a slight imbalance of the total mass losses past these two depths. A net adsorption of 1.45 E x 10^3/ha

Table 4.20. Total elemental loss and ion mass balance for field and laboratory column studies after 100 cm irrigated acid rain for three treatments

Tmt. pH		Depth (cm) 15 cm Column	 Field	 75 cm Column	 Field
		---------- kg/ha ----------			
3.0	+	157.9	173.6	149.4	125.7
	-	497.6	404.5	368.2	230.0
	±	655.5	578.1	517.6	355.7
3.7	+	63.9	115.3	75.8	113.9
	-	212.8	181.2	189.9	149.0
	±	276.7	296.5	265.7	262.9
4.6	+	55.7	99.6	56.8	99.3
	-	126.1	136.8	129.1	104.0
	±	181.8	236.4	185.9	203.3
TOTAL	+	297.5	388.5	282.0	338.9
	-	854.5	722.6	686.2	483.0
	±	1152	1111	968	822
		---------- E x 10^3/ha ----------			
3.0	+	12.25	9.63	9.52	6.21
	-	11.95	9.35	9.59	5.72
	±	24.20	18.68	19.11	11.93
3.7	+	5.27	5.51	4.07	5.42
	-	5.19	4.38	4.94	3.77
	±	10.46	9.89	9.01	9.19
4.6	+	2.94	4.60	2.87	4.60
	-	3.17	3.42	3.30	2.80
	±	6.11	7.99	6.17	7.40
TOTAL	+	20.46	19.64	16.46	16.23
	-	20.31	17.15	17.83	12.29
	+	40.77	36.79	34.29	28.52

+ = sum of cations

- = sum of anions

± = sum of cations and anions

occurred in the 15-75 cm depth compared with the 0-15 cm depth (being 9.01 and 10.46 E x 10^3/ha, respectively). The 3.7 treatment caused an increased loss of cations of 2.33 E x 10^3/ha compared with the control for the 15 cm depth. However, a portion of this loss was readsorbed in the 15 to 75 cm depth.

For the 3.0 treatment, much higher losses occurred for both depths, totalling 24.20 and 19.41 E x 10^3/ha, respectively. There was not only a further large loss of cations, but there was also a redistribution of the ions in the 15 to 75 cm depth resulting in an overall adsorption of 21 percent of the ions passing the 15 cm depth.

Field experiment

The field experiment showed similar trends on the mass balance and losses with increasing soil acidity at depth. However, the field control data showed elevated losses of ions when compared with the column control data. This could be explained as natural additions in the field from rainfall, throughfall, litterfall, etc., that were continually being added to the soil over the six month period of the field experiment.

In addition, the incremental additions of rainfall in the field with the resulting postirrigation readjustments in equilibrium plus the water flux patterns for the soil for 6 cm rainfall would tend to retain more ions in the upper soil region under these unsaturated conditions. These somewhat opposing phenomena resulted in elevated losses compared with the column control data, but decreased losses with acid treatments when compared with the column data.

For the control, 7.99 and 7.40 E x 10^3/ha of ions moved to the 15 and 75 cm depth, respectively, which were slightly elevated above the column control losses. For the 3.7 treatment, the losses at the 15 and 75 cm depths were 9.88 and 9.19 E x 10^3/ha, respectively. The adsorption in the 15 and 75 cm depths for the control and 3.7 treatments of the quantities that passed the 15 cm depth were similar, being 0.59 and 0.80 E x 10^3/ha, respectively. However, the overall losses past 15 and 75 cm for the 3.7 treatment were slightly less for the field experiment than for the corresponding 75 cm column experiment. This indicated good agreement between the field and column experiments for the two depths for the 3.7 pH treatment.

For the 3.0 treatment for the 15 and 75 cm depth, 18.88 and 11.93 E x 10^3/ha, respectively, were lost. When compared with the column experiments, the 15 cm depth showed a 21 percent decrease in ion loss and the 75 cm depth showed a 38 percent ion loss, despite the additions of ions under natural conditions in the field. This indicated the modifying forces in the field conditions that tend to retain at depth the mobilized ions from the surface soil region when compared with the loss of ions from a column study.

Column vs field

When comparing column versus field data, the 3.0 column treatment removed slightly more ions than the 3.0 field treatment at the 15 cm depth. This was more pronounced at the 75 cm depth. This indicated that the column experiment was better correlated with the field experiment for the 15 cm than the 75 cm depth for the 3.0 treatment when the elemental loss is expressed on a kg/ha basis.

When comparing the 3.7 pH treatments, the data showed that there was good agreement between the field and column results regarding elemental losses below the 15 cm depths (314 vs 297 kg/ha) and 75 cm depth (256 vs 263 kg/ha), respectively.

For the control data, the column loss was less than the field loss. This could be explained by the fact that small continual additions were being made to the soil under natural field conditions during the irrigation period of 6 months, whereas the column experiments were conducted under closed conditions.

There was an overall uniform movement of cations with depth for the three treatments. For 3.0, these movements of ions for the 15 and 75 cm depth were 158 and 149 kg/ha for the column, 64 and 76 kg/ha for the 3.7 column treatment, and 56 and 57 kg/ha for the control expressed as kg/ha. For the field data, the movement of ions past these two depths for the three treatments were 174 and 126, 115 and 114, and 99 and 99 kg/ha, respectively.

Summing all treatments indicated that for the 15 cm depth, both field and column experiments had approximately the same elemental loss (1152 and 1111 kg/ha, respectively). For the 75 cm depth, the elemental loss was 968 and 822 kg/ha, respectively.

The field loss past the 15 cm depth for the 3.0 treatment was 78 percent of the column loss. For the 75 cm depth, the field loss was 66 percent that of the column loss.

For the 3.7 treatment, the field loss past the 15 cm depth was 91 percent that of the column. For the 75 cm depth, the field loss was 102 percent that of the column loss. There was much better agreement between the column and field data for both depths in the case of the 3.7 treatment than the 3.0 treatment. For the control, the field experiment showed a movement past the 15 cm depth of 130 percent that of the column experiment. For the 75 cm depth, the field experiment showed a movement of 119 percent that of the column experiment. This elevated movement in the field compared to the column could very well be due to the interirrigation additions of the ions that occurred naturally in the rain and throughfall and weathering processes.

Summing over treatment (3.0, 3.7, and 4.6), and comparing column vs field, for the 15 cm depth, the field loss was 88 percent that of the column. For the 75 cm depth, the field loss was 82 percent that of the column experiment.

The net adsorption (treatment minus control) for the column 15 to 75 cm depth for 3.0 pH treatment was 5.32 E x 10^3/ha and for the field pH 3.0 treatment was 6.12 E x 10^3/ha. This was very good agreement indicating again the value of net calculations. For the 3.7 pH treatment, the column and field net adsorption for the 15 to 75 cm depth were 1.96 and 0.13 E x 10^3/ha, respectively. For the cations only, the adsorption in the 15 to 75 cm depth at 3.0 pH for column and field were 2.68 and 2.81 E x 10^3/ha, respectively, and very low for the 3.7 treatment. The field study was comparative to the column laboratory study in some cases both for a description and magnitude of ion balance and losses, and in more acid conditions, was more descriptive than quantitative. Descriptive comparisons of ion balance and losses with depth and treatment were similar for the field and laboratory studies. Quantitative adsorption with depth was 16 percent overall for column and 22 percent overall for field.

Mobility and Adsorption

Sulfate

Sulfate was the major anion added in the acid rain treatments. The control treatment (4.65 pH) contained 1.54 E x 10^3/ha, the 3.7 pH treatment 2.89 E x 10^3/ha, and the 3.0 pH treatment 8.76 E x 10^3/ha (Table 4.21).

Column. For the control at 15 cm, 0.37 E x 10^3/ha were adsorbed or 24 percent of that added in the rain to the soil surface. This corresponded to 17.7 kg/ha. For the 3.7 treatment, 0.41 E x 10^3/ha were adsorbed (19.6 kg/ha) or 14.2 percent of that added in the acid rain. For the 3.0 treatment, 0.54 E x 10^3/ha were adsorbed (25.8 kg/ha) or 6.2 percent of that added in the acid rain.

For the 75 cm depth, a much higher proportion of the sulfate was adsorbed indicating increased adsorption in the Candler soil with depth. For the control treatment, 0.54 E x 10^3/ha (27.5 kg/ha) were adsorbed or 35 percent of the amount of sulfate added to the soil in the acid rain. For the 3.7 treatment, 1.14 E x 10^3/ha (54.8 kg/ha) were adsorbed or 38 percent of the amount added in the acid rain. For the 3.0 treatment, 4.09 E x 10^3/ha were adsorbed (196.5 kg/ha) or 46.7 percent of that added in the acid rain.

Table 4.21. Loss of sulfate, nitrate, and hydrogen in the Candler soil after 100 cm irrigated acid rain in the field and column studies.

ION	Treatment pH	Add/Loss	Depth (cm)	Column Kg/ha	Column Kg/ha Ads	Column Kmol^{c}/ha	Column Kmol^{c}/ha Ads	Field Kg/ha	Field Kg/ha Ads	Field Kmol^{c}/ha	Field Kmol^{c}/ha Ads	% Adsorbed Column	% Adsorbed Field
SO_4	3.0	Total Add		420		8.75		420		8.75			
		Loss	15	384.2	35.8	8.21	0.54	326.0	94.0	6.79	1.96	8.5	22.4
			75	223.5	196.5	4.66	4.09	143.2	276.7	3.00	5.72	46.7	65.8
			15-75		170.7		3.55		182.7		3.76	40.6	43.0
	3.2	Total Add		136.7		2.99		136.2		2.86			
		Loss	15	119.1	19.9	2.48	0.41	115.1	23.9	2.40	0.49	14.2	12.0
			72	83.9	54.0	1.71	1.14	83.8	54.9	1.75	1.19	39.4	39.4
			15-75		35.2		0.73		31.3		0.92	25.4	22.6
	4.6	Total Add		73.6		1.54		73.6		1.54			
		Loss	15	55.9	17.2	1.19	0.37	71.9	2.0	1.49	0.04	24.0	2.3
			75	47.9	25.2	1.00	0.54	44.4	29.2	0.92	0.41	35.1	39.6
			15-75		8.0		0.17		27.2		0.37	10.9	36.9
NO_3-N	3.0	Total Add		20.4		1.45		20.4		1.45			
		Loss	12	18.2	1.2	1.36	0.19	2.8	12.9	0.56	0.97	8.3	41.0
			75	21.1	0.2	1.52	0.00	7.2	13.2	0.51	1.00	1.5	64.2
	3.2	Total Add		2.0		0.36		5.0		0.38			
		Loss	15	2.0	3.0	0.14	0.21	2.2	2.8	0.16	0.20	60.0	54.0
			75	4.2	0.3	0.36	0.00	3.2	1.2	0.26	0.06	6.0	26.0
	4.6	Total Add		1.41		0.10		1.41		0.10			
		Loss	12	0.51	0.90	0.04	0.06	1.85	-0.44	0.16	-0.08	63.0	-36.0
			72	0.36	1.05	0.00	0.06	3.2	-1.79	0.23	-0.13	74.5	-122.0
H	3.0	Total Add		10.0		10.0		10.0		10.0			
		Loss	15	0.80	9.2	0.80	9.20	0.14	9.86	0.14	9.86	92.1	98.9
			75	0.45	9.55	0.45	9.55	0.01	9.99	0.01	9.99	95.5	99.9
	3.2	Total Add		2.00		2.00		2.00		2.00			
			12	0.30	1.70	0.30	1.70	.03	1.97	0.03	1.97	85.0	98.2
			75	0.12	1.88	0.12	1.88	.01	1.99	0.01	1.99	94.0	99.5
	4.9	Total Add		0.23		0.22		0.23		0.23			
		Loss	15	0.14	0.09	0.12	0.10	.006	0.23	0.006	0.23	43.4	98.3
			75	0.08	0.15	0.06	0.12	.001	0.23	0.001	0.23	65.2	98.6

For the 15 cm depth, there was a decreasing percentage of sulfate adsorption as the pH decreased and sulfate concentration increased. For the 75 cm depth, the reverse trend occurred. Thus for low concentrations (4.65 pH) of sulfate additions in the rain to the Candler soil, the 0 to 15 cm depth adsorbed 31 percent of the amount that was adsorbed in the 0 to 75 cm depth. As the rain pH decreased, sulfate concentration increased and the 15 to 75 cm depth became more instrumental in sulfate adsorption, adsorbing 64 percent of the total sulfate adsorbed in the 0 to 75 cm depth for the 3.7 treatment, and 87 percent of the total sulfate adsorbed for the 3.0 treatment. However, more than 50 percent of the added sulfate had moved below the 75 cm depth for all treatments. In the case of the 3.0 treatment, this corresponded to 223.5 kg sulfate moving in the percolating soil solution. Considering the very low exchange capacities with depth, it is not unreasonable to conclude that the sulfate could move to much greater depths before it is totally adsorbed. In fact, a soil 75 cm in depth corresponded to a concentric ring of land around the lake which extended 5.76 (19') from the edge of the lake and which would be contributing the described amounts of sulfate, Al, and other cations to the water table. Water flux data from another part of the field experiment (see Chapter 4, the first and second parts of the third section) showed that the vertical flow to the water table and the horizontal movement of ions in the mounded wave moved rapidly towards the lake.

Field For the control at 15 cm, 0.04 E x 10^3/ha (or 2.0 kg/ha) were adsorbed or 3 percent of that added in the rain. For the 3.7 treatment, 0.49 E x 10^3/ha (23.6 kg/ha) were adsorbed or 17 percent of the amount added in the rain. For the 3.0 treatment, 1.96 E x 10^3/ha (94.0 kg/ha) were adsorbed or 22 percent of the amount added in the rain.

For the 75 cm depth, a much higher proportion of the sulfate was adsorbed indicating increased SO_4 adsorption with depth. For the control, 0.61 E x 10^3/ha (29.3 kg/ha) were adsorbed or 39.6 percent of that added in the rain. For the 3.7 treatment, 1.14 E x 10^3/ha (54.9 kg/ha) were adsorbed or 39.4 percent of that added in the rain. For the 3.0 treatment, 5.72 (274 kg/ha) were adsorbed or 65.4 percent of that added in the rain.

Column vs field. Sulfate adsorption in the field experiment showed similar trends as the column experiment. The percent adsorption in the field at 75 cm for the control was 39.6 (35.1 for column), for the 3.7 treatment was 39.5 (39.4 for the column), and for the 3.0 was 65.4 (46.7 for the column). Thus both column and field study compared well in the magnitude of sulfate adsorption. For the 15 cm depth, the corresponding field (column) data were 24.0 (3.3) for control, 14.2 (17.0) for 3.7, and 6.2 (22.4) for 3.0 pH treatments, respectively.

The figures for net sulfate adsorption (Table 4.22) showed that much more adsorption occurred in the field than in the columns (1.92 vs 0.17 E x 10^3/ha, respectively) at the 15 cm depth for the pH 3.0 treatment. Although both field and column had the same input of sulfate, the pulsing of the rain in 5 cm intervals resulted in more adsorption due to the pattern of water movement in the soil. The hydraulic characteristics for a 5 cm rain showed that the water moved to the 15 cm depth and slowed with depth. The sulfate was adsorbed during this time of drying and evacuation of the soil pores. Whereas, in the column, the

Table 4.22 Net adsorption[1] of three major ions by the Candler soil after 100 cm irrigated acid rain in column and field studies

		COLUMN		FIELD	
ION	DEPTH (cm)	3.0 pH	3.7 pH	3.0 pH	3.7 pH
		E x 10^3/ha			
SO_4	0-15	0.17	0.04	1.92	0.45
	15-75	3.38	0.56	3.19	0.08
	0-75	3.55	0.60	5.11	0.53
	Input	8.75	2.89	8.75	2.89
NO_3-N	0-15	0.13	0.15	1.01	0.26
	15-75	-0.19	-0.21	0.13	0.04
	0-75	-0.06	-0.06	1.14	0.22
	Input	1.45	0.36	1.45	0.36
H	0-15	9.11	1.60	9.63	1.74
	15-75	0.29	0.13	0.13	0.02
	0-75	9.40	1.73	9.76	1.76
	Input	10.0	2.0	10.0	2.0

[1] treatment minus control

constant head moved the sulfate below the 15 cm depth and adsorption occurred at a greater depth. Thus the water flow characteristics and rate of application influence the depth of sulfate adsorption more than the actual differential (or uniformity) in adsorptive capacity of the soil with depth. The same trend occurred for the 75 cm depth. Here, the magnitude of adsorption was much greater (5.11 for field and 3.55 E x 10^3/ha, respectively, for column). However, the magnitude of difference between the column and field remained the same for each depth being 1.75 E x 10^3/ha for 15 cm depth and 1.56 E x 10^3/ha for 75 cm depth. The net adsorption in the 15 to 75 cm depth for the column and field were 3.38 and 3.19 E x 10^3/ha indicating similar net adsorption of SO_4.

For the column and field for 3.7 pH, there was uniform net adsorption at 0.60 and 0.53 E x 10^3/ha, respectively, for the 75 cm depth. For the 15 cm depth, the net adsorption was 0.04 and 0.45 E x 10^3/ha for the column and field, respectively. The net adsorption in the 15 to 75 cm depth for column and field were 0.56 and 0.08 E x 10^3/ha, respectively. Thus, for the 3.7 pH treatment, although the total SO_4 adsorbed in the 0-75 cm depth was similar for column and field, the adsorption in the profile differed with depth. Similarly for 3.0 pH treatment

Nitrate-N

In the 3.0 column there was little evidence of nitrate adsorption, expecially at the 75 cm depth where 98.7 percent of the added nitrate was recovered in the leachate. At the 15 cm depth, there was a loss of 12 percent (88 percent recovery) of the added nitrate. This could be a loss by anion exchange in the organic top layer of soil in the column. However, the field data showed that the 15 and 75 cm depth adsorbed 63 and 66 percent, respectively, of the nitrate added in the acid rain. This was despite the amounts that would be expected to occur as added nitrate from the ambient rainfall and throughfall and windblown materials. The net loss could very well be due merely to uptake by tree and plant roots and conversion and utilization by soil microorganisms.

For the 3.7 treatment at the 75 cm depth for the column, there was 94 percent recovery of the nitrate. However, the percentage recovery of the nitrate in the 15 cm depth was 60 percent, although the adsorbed amount was very close to that of the 3.0 treatment. This would indicate that the soil was indeed adsorbing a definite amount of nitrate regardless of the amount added in excess, the soil adsorbing 0.19 and 0.21 E x 10^3/ha in the column, for 3.0 and 3.7 treatment, respectively. However, rather than being true adsorption, the organisms present could also be utilizing the nitrate or converting it, even though the column extractions were completed in about 48 hours. The column data did show that with time there was a period of denitrification.

For the control, there was essentially no adsorption of nitrate (Table 4.21). In the field, more nitrate was found than was actually applied in the rain. This indicated that there was nitrate accumulation, especially at depth probably due to microbial activity. In fact, more than twice the amount of added nitrate was found at the 75 cm depth (i.e., 0.23 vs 0.10 E x 10^3/ha added).

Hydrogen

For the pH 3.0 acid rain, 1 me/L or 10 E x 10^3/ha or H^+ was added to the soil surface in the 100 cm acid rain. In the 15 cm depth in the column, 9.2 E x 10^3/ha or 92 percent was adsorbed. At the 75 cm depth, 95.5 percent was adsorbed. In the field, 98.6 percent was adsorbed at 15 cm and 99.9 percent at 75 cm. However, there was enough of a differential in adsorption to show a marked difference in pH of the soil solutions between field and column, the column leachates being lower in pH than the field leachates.

For 3.7 pH in the column, 85 percent of H^+ was adsorbed in 15 cm and 94 percent by 75 cm depth. The corresponding figures for the field were 98.6 and 99.5 percent, respectively. Although there was less H adsorbed (as percent) by the pH 3.7 treatment at 15 cm compared to the 3.0 pH treatment, the soil solution was not more acidic since there was correspondingly less H added in the pH 3.7 treatment, the differential being 5.7 times less H. At pH 4.6 (control treatment), the percent recoveries were even lower. However, again, there was essentially so little H in solution that the pH was well above the treatments.

In summary, sulfate was freely adsorbed, the mechanism apparently more dependent on hydraulic characteristics and rate of rain application than adsorptive capacity of the soil. The dynamics of nitrate conversions, utilization and slight possible adsorption, as well as accumulation with depth, make the results on nitrate adsorption to be inconclusive. Adsorption was probably minimal from the data. Hydrogen was highly adsorbed and acted as the major replacing cation in an acid rain system. Net H adsorbed for the field and column were in close agreement (Table 4.12). At 15 cm for the 3.0 treatment, the field and column adsorbed 9.63 and 9.11 E x 10^3/ha, respectively. For 3.7 treatment, the corresponding figures were 1.74 and 1.61 E x 10^3/ha, respectively. At 75 cm, for 3.0 pH, the net adsorption in the field and column were 9.76 and 9.40 E x 10^3/ha, respectively. For the 3.7 pH, the corresponding adsorption figures were 1.76 and 1.73 E x 10^3/ha, respectively.

Hydrogen adsorption and cation balance

The major cation in both treatments 3.7 and 3.0 pH acid rain treatments was hydrogen. At 3.0 pH, hydrogen dominated the total of all other input cations by almost four times. These other cations in the acid rain existed as background cations from the lake water that was used as an irrigation source. The difference in the input H and the output H would be an estimate of the H adsorption. Likewise, the difference in the input and output values for each of the cations would be an estimate of the displacement of these ions, presumably by the dominant H ion in the system. Thus, the sum of the cations lost from the 15 and 75 cm depth would be an estimate of the H (E x 10^3/ha) adsorbed in their displacement. That sum subtracted from the total H adsorbed would be an estimate of the hydrogen adsorbed by other sites (e.g., organic matter) plus the readsorption of a portion of the cations (e.g., Al), prior to the respective 15 and 75 cm depths.

Column. For the control treatment at both 15 and 75 cm depths, the net cation output was zero (Table 4.23). This indicated that there

Table 4.23. Relationship between hydrogen input and cation loss for three acid rain treatments at two depths in soil columns.

Depth	Ion	3.0			3.7			4.6		
		Input	Output	Net Loss[1]	Input	Output	Net Loss	Input	Output	Net Loss
		E x 10^3/ha								
15 cm	H	10.0	0.60	-9.2	2.0	0.30	-1.70	0.23	0.14	-.09
	Ca	0.64	2.18	1.54	0.64	0.88	0.24	0.64	0.36	-.28
	Mg	0.71	1.20	0.49	0.71	0.97	0.26	0.71	0.58	-.13
	K	0.11	0.21	0.10	0.11	0.20	0.09	0.11	0.20	-.09
	Na	1.33	1.43	0.10	1.33	1.43	0.10	1.33	1.33	0
	Al	0.02	6.43	6.42	0.01	1.49	1.48	0.01	0.33	+.32
Total Cations		2.60	11.45	8.65	2.80	4.97	2.17	2.80	2.80	0
75 cm	H	10.0	0.45	-9.55	2.0	0.12	-1.88	0.23	0.08	-0.15
	Ca	0.64	3.46	2.82	0.84	1.37	0.73	0.64	0.91	+0.27
	Mg	0.71	1.13	0.42	0.71	0.76	0.05	0.71	0.35	-0.36
	K	0.11	0.16	0.05	0.11	0.14	0.03	0.11	0.11	0
	Na	1.33	1.46	0.13	1.33	1.34	0.01	1.33	1.23	-0.10
	Al	0.01	2.92	2.91	0.01	0.28	0.27	0.01	0.19	0.18
Total Cations		12.80	9.13	6.34	2.80	3.89	1.09	2.80	2.79	-.01

[1] net loss = Output - Input, if negative, adsorption occurred

was no net loss of cations in excess of the input cations in the acid rain. The H added in the acid rain control at pH 4.65 was very low quantity and the overall effect was minimal.

For the 3.7 treatment, the H loss past the 15 cm depth was 0.30 E x 10^3/ha for an adsorption of 1.7 E x 10^3/ha or 85 percent of the H added. The loss of cations was in excess of that amount due mostly to the loss of Al as the pH of the soil decreased from the effect of the acid rain. For the 75 cm depth, the H^+ adsorption had increased to 1.88 E x 10^3/ha or 94 percent of the added H in the acid rain. The loss of cations past the 75 cm depth was 1.09 E x 10^3/ha.

For the pH 3.0 treatment for 15 cm depth, the adsorbed H was 9.2 E x 10^3/ha or 92 percent of the added H in the acid rain of 10 E x 10^3/ha. The net cations lost were 8.65 E x 10^3/ha or 94 percent of the hydrogen adsorbed. The difference (0.55 E x 10^3/ha) of adsorbed H was possibly in the organic matter phase. For the 75 cm depth, 9.55 E x 10^3/ha were adsorbed or 95.5 percent of the H added in the acid rain. The cation adsorption was 6.34 E x 10^3/ha or 66 percent of the adsorbed H. The difference 3.22 E x 10^3/ha could be H adsorbed by other sites in the soil, readsorption or precipitation of cations in this soil region, or microorganism reactions. The Ca and Al were the dominant cations exchanged by the H^+ in the 3.0 and 3.7 treatments.

For the 3.0 treatment, the difference in the Al lost at the 15 and 75 cm depth was 3.61 E x 10^3/ha which corresponded well with the imbalance in the H-cation exchanges of 3.22 x 10^3/ha. Thus the immobilization of Al in the 15 to 75 cm depth accounted for excess H and thus it appeared that very little H was lost or adsorbed in nonexchange reactions such as adsorption by the organic matter sites. For the 3.7 treatment, Al immobilization of 1.21 E x 10^3/ha in the 15 to 75 cm depth also accounted for any nonexchange H losses. Even for the control, Al immobilization was 0.14 E x 10^3/ha in the 15-75 cm depth which accounted for the H imbalance (nonexchange reactions) of 0.06 E x 10^3/ha.

Field. A similar approach comparing the mass balance between H adsorption and cation loss for the field showed similar data (Table 4.24). At the 15 cm depth for 3.0 pH treatment, the net difference between the H and the cations was 1.98 E x 10^3/ha indicating a negative balance for cations. For the 75 cm depth, there was a net difference of 5.33 E x 10^3/ha between the H adsorbed and the total cation loss. However, adsorption of cations in the 15 to 75 cm depth was 3.29 E x 10^3/ha with Ca and Al composing 89 percent of the adsorption. Thus the sum of cation loss plus cation adsorption equalled 6.64 E x 10^3/ha. The total cation loss at 15 cm was also 6.64 showing the good agreement resulting from the analytical data for the columns for these two depths. Net H adsorption for the two depths 15 cm and 75 cm were 8.62 and 8.68 E x 10^3/ha, respectively. Thus for the 3.0 treatment there was a 25 percent deficit in cation loss unaccounted for compared to the adsorbed H.

For the 3.7 treatment for the field data, the 15 cm net cation loss was 2.72 E x 10^3/ha and that for the 75 cm depth was 2.52 E x 10^3/ha with the difference of 0.20 E x 10^3/ha accounted for in adsorption of the cations. The H adsorption for the two depths were 1.96 and 1.96 E x 10^3/ha, respectively, showing a slight excess of cations possibly added from extraneous sources.

Table 4.24. Relationship between hydrogen input and cation loss for three acid rain treatments at two depths under field conditions

Depth	Ion	3.0			3.7			4.7		
		Input	Output	Net Loss[1]	Input	Output	Net Loss	Input	Output	Net Loss
		$E \times 10^3$/ha								
15 cm	H	8.71	0.09	-8.62	1.98	.02	-1.96	0.23	0.01	-0.22
	Ca	0.64	4.21	3.57	0.64	2.30	1.66	0.64	1.76	1.12
	Mg	0.71	1.49	0.79	0.71	0.85	0.14	0.71	0.64	-0.07
	K	0.11	0.43	0.32	0.11	0.39	0.28	0.11	0.43	0.32
	Na	1.33	1.75	0.42	1.33	1.85	0.52	1.33	1.71	0.38
	Al	0.01	1.56	1.55	0.01	0.13	0.12	0.01	0.05	.04
Total Cations		2.80	9.44	6.64	2.80	5.62	2.72	2.80	4.59	1.79
75 cm	H	8.71	.03	-8.68	1.98	.02	-1.96	0.23	0.01	-0.22
	Ca	0.64	2.80	2.16	0.64	2.41	1.77	0.64	1.82	1.18
	Mg	0.71	1.25	0.54	0.71	0.77	.06	0.71	0.63	-0.08
	K	0.11	0.39	0.28	0.11	0.30	.21	0.11	0.45	0.34
	Na	1.33	1.69	0.33	1.33	1.79	.44	1.33	1.66	0.33
	Al	0.01	0.05	0.04	0.01	.06	.04	0.01	0.03	0.02
Total Cations		2.80	6.18	3.35	2.80	5.32	2.52	2.80	4.59	1.79

[1] net loss = Output - Input, if negative, adsorption occurred

Aluminum mobility

Table 4.25 shows the mobility of aluminum in the Candler Typic Quartzipsamment moving past the two depths 15 and 75 cm after treatment of 100 cm acid rain at three pH levels (3.0, 3.7, and 4.6). All three treatments moved Al past both depths in the column study. The field study showed the same trend and it is clear that Al is continually being lost below these depths even during natural rain events.

In the columns, 0.33 E x 10^3/ha was removed from the 0-15 cm depth by the control treatment. This corresponded to 0.032 mg/L in the soil solution. The 3.7 treatment removed 1.49 E x 10^3/ha from the 0-15 cm depth, which was 4.5 times the amount removed by the control rain at pH 4.65, and corresponded to 0.15 mg/L. The 3.0 treatment removed 5.43 E x 10^3/ha which corresponded to 0.64 mg/L or about 20 times the amount removed by the control.

Less Al moved from the soil at 75 cm than from the 15 cm depth for all treatments. The Al removed from the upper 0-15 cm layer of soil was obviously partially immobilized in the 15 to 75 cm region of the profile. For 4.6 pH treatment 0.19 E x 10^3/ha was removed below 75 cm which was an adsorption of 42 percent of the Al that moved past 15 cm. The 3.7 treatment moved 0.28 E x 10^3/ha past 75 cm for a much higher percentage (81 percent) of that moved past the 15 cm depth. In the case of the 3.0 treatment, a large amount, 2.92 E x 10^3/ha moved below 75 cm depth which was 45 percent of that moved past the 15 cm depth. This indicated that the 3.0 pH treatment removed large quantities of Al from the 0 to 15 cm depth and the Candler soil immobilized 55 percent of this

Table 4.25. Aluminum mobility and its relationship to cation exchange capacity after 100 cm irrigated acid rain for three treatments

Depth	Cation exchange capacity E x 10^3/ha	Acid rain tmt pH	Aluminum loss E x 10^3/ha	kg/ha	% of CEC
15	87.2	3.0	6.43	57.9	7.37
		3.7	1.49	13.4	1.71
		4.6	0.33	3.0	0.38
75	271.2	3.0	2.92	26.3	1.08
		3.7	0.28	2.5	0.10
		4.6	0.19	1.7	0.07

soluble Al by 75 cm depth. However, it is important to note that 45 percent did move past the 75 cm depth and thus to the water table in the zone near the lake.

In order to put into perspective the magnitude of the Al mobility, a direct comparison can be made with the CEC. The Candler soil has a low cation exchange capacity in the surface 15 cm of 3.97 mE/100 g and in the surface 75 cm of 2.27 mE/100 g. Thus the CEC decreases with depth. The base saturation is also very low, being 2.77 and 2.64 percent for the surface 15 and surface 75 cm, respectively.

The 3.0 pH treatment at 15 cm removed 6.43 E x 10^3/ha which represented 7.4 percent of the CEC. Corresponding percentages for the 3.0 pH at 75 cm, 3.7 pH at 15 and 75 cm were 1.1, 1.7, and 0.1 percent, respectively. Since Al comprises about 96 percent of the CEC, only a small fraction of the total Al had been removed at these two depths (Table 4.25).

Ion Net Loss Column vs Field

One of the considerations for conducting laboratory column and field irrigations of acid rain was to assess whether there would be any agreement or correlation of data for these two approaches which would be of practical value in assessing ion mobility. Basically, the field experiment applied intermittent rain to unsaturated soil under natural conditions where additions from ambient rain, throughfall, microbial action, etc., were free to proceed. Thus the rain was pulsed onto the soil which allowed for drying and more importantly, incomplete penetration into the soil, allowing more time for equilibrium conditions to be reestablished. The column acid rain was applied over a short period of time under saturated conditions in controlled closed environment under constant head.

A few suppositions could be made by looking at the data to explain logical and opposing processes that take place under field conditions. Natural additions of ions from rain, throughfall and stemflow, leaves, soil, animals, microorganisms, wind, erosion, and weathering all add nutrients to the soil. However, adding rain at relatively low intermittent quantities does not allow for the removal of these additions, especially at depth, since less than the applied amounts of rain move to depth and in a decreasing manner. It is thus not unreasonable to conclude that certain combinations of depth, rate of application, time of sampling, depth of sampling, amount of rain applied, and soil characteristics unique to each soil will more closely approximate a set of equally specific lab conditions. Both the field and column studies were conducted with these in mind, choosing the most reasonable practical combination of parameters from both laboratory and field considerations.

The results agree according to the elemental or nutrient parameters chosen for comparison. Considering the mass balance or sum of cations and anions on a kg/ha or E x 10^3/ha basis, several conclusions can be drawn. In 1981, the application rate was 2.5 cm/hr for a total of 50 cm rain. For 1982, the same rate was used but the duration of rain event was for two hours, totalling 100 cm rain. Subsequent flux experimental data indicated the differential movement of water in the Typic Quartzipsamment for these two quantities of applied rain. In addition, nature controlled the weather and 1981 was a dry year but

1982 was an exceptionally wet year. Thus we have a low application amount per event in a dry year as opposed to a larger application amount per event in a wet year. We would expect differences to occur in the total quantities of ions moved beyond 15 and 75 cm depths.

Comparisons can be made using data for total quantities lost for the treatments or for net amounts los (treatment minus control). These comparisons give different interpretations if considering the treatment alone. It is more reasonable to consider net loss by nullifying control (natural) conditions that occurred for the two years.

For the field data, since 1981 samples were not as extensively analyzed as 1982, only the main nutrient ions will be compared. They are the sum of the Ca, Mg, K, SO_4, and NO_3-N. Also, only pH 3.7 treatment was applied in 1981, thus only this treatment will be considered.

For the column, the sum of ions in kg/ha moving past the 15 cm depth was 97 kg/ha (Table 4.26). The corresponding loss for 1981 at the 15 cm depth was 85 kg/ha and for 1982 was 55 kg/ha. This indicated that the 1981 data for lower amount of added rainfall agreed better with the column data at 15 cm depth. The 1981 field experiment mobilized 88 percent of the major nutrient ions which were mobilized by the column experiment. This can be explained since 1981 had application amounts of 2.5 cm per irrigation event. The water flux diagrams showed that the volumetric wetting water front only increased appreciably in the 0-15 cm depth while the soil was draining. Thus the ions that had been mobilized in the 0 to 15 cm depth moved in a much restricted water column below about 20 cm to the 75 cm depth and below. This would restrict the capacity of the water column to move the ions to lower depths.

Table 4.26. Comparison for two years of net ion loss for two treatments at two depths.

	Treatment pH	Total ion loss*				Net ion loss**			
		Depth (cm)							
		15	75	15	75	15	75	15	75
		---kg/ha---		--Ex10^3/ha--		---kg/ha---		--Ex10^3/ha--	
1981 Field	3.7	274	129	8.15	4.75	85	27	2.28	1.08
	4.6	189	102	5.67	3.67				
1982 Field	3.7	189	161	6.13	5.62	55	49	1.64	1.48
	4.6	134	110	4.49	4.14				
1982 Column	3.7	176	131	5.04	4.36	97	56	2.69	1.95
	4.6	79	75	2.35	2.43				
		Adjusted ion loss***				Adjusted net ion loss***			
1981 Field	3.7	265	89	7.66	3.26	83	19	2.20	0.74
	4.6	182	70	5.66	2.52				
1982 Field	3.7	186	135	6.02	4.73	54	42	1.61	1.24
	4.6	132	93	4.41	3.48				

*Ca, Mg, K, SO_4, and NO_3-N

**3.7 treatment minus 4.6 treatment (control)

***total ion loss x factor in Table 4.5

i e , to 75 cm Thus a higher proportion of the mobilized ions would move past 15 cm but correspondingly less past 75 cm.

For the column, the sum of ions moving past 75 cm depth was 56 kg/ha. For the field at 75 cm depth, the ion loss for 1981 was 27 kg/ha and for 1982, the loss was 49 kg/ha Thus the 1982 data compared better with the column data for loss past 75 cm (55 kg/ha) than the 1981 field data (27 kg/ha). By coincidence, the 1982 field loss was 88 percent of the column loss past 75 cm. This again can be partly explained merely by the nature of the water flux characteristics for 2 5 and 5 cm rain. The 5 0 cm rain moved the high volumetric water content to just past the 75 cm depth Thus the ions mobilized in the 0 to 15 cm depth were free to readily be carried to greater depths due to the lower tension exerted, and the equilibrium forces imposed. Thus there was correspondingly more ion mobility past the 15 cm depth and thus on past the 75 cm depth.

The ion concentrations were slightly higher in the 1981 soil solutions than the 1982 soil solutions, again the result of drier soil conditions and lower amounts of rain in the rainfall events applied

When converting the kg/ha data to E x 10^3/ha, the corresponding loss past 15 cm depth for 1981 was 86 percent of the column experiment. For the 75 cm depth, the corresponding losses for 1982 were 77 percent that of the column experiment Thus whether considering quantity (kg) or equivalent losses, the same conclusions can be drawn.

A further adjustment was made to the field data since less than 100 percent of the applied rain moved past these two depths (Table 3.4). The result was a lower net movement of water past 15 cm and 75 cm with correspondingly lower net ion loss especially in the 75 cm depth when expressed as the adjusted net ion loss

CHAPTER 6
CONCLUSIONS

Ion Movement

The two treatments 3.0 pH and 3.7 pH did not affect the soil ions in the same manner, i.e., each ion was unique in its response to the acid rain treatments. These differences were seen in time response, e.g., Mg was more rapid in response to acid rain than Ca, magnitude of response, e.g., Ca was removed in greater quantities than Mg, uniformity of response, e.g., K was steadily leached throughout the irrigation period whereas Ca and Mg were leached early in the irrigations and decreased with additions of acid rain. Potassium also showed rapid resupply characteristics, fast recovery after a rain event, and little treatment affect and depth effect

There were also differences in the effects manifested between the treatments. The 3.0 pH treatment had a greater ion leaching effect than the 3.7 pH. However, the effects were not uniform for all parameters, e.g., there were large treatment differences for Ca and Mg, but little differences for NH_4-N and K, with Al showing very large differences in mobilization by the treatments

There were also treatment differences when considering the valence of the mobilized cations, e.g., for the divalent cations Ca^{++} and Mg^{++}, the treatment differences were much greater than for K^+, whereas for the Al^{3+} the treatment differences were very large.

The treatment differences were also clearly evident with depth, e.g., the divalent cations removed at the 15 cm depth were partially adsorbed by 75 cm depth. For the trivalent Al, there was a much higher readsorption percentage with depth, while for K depth had little effect.

The ion fronts could be observed as they moved to depth with time. Magnesium was especially mobile in this regard. The fronts for Ca and Mg were clearly decreasing by the end of 100 cm application even for the 3.0 pH treatment. This indicated that maximum leaching of these elements had occurred before the 100 cm had been reached and that an equilibrium was being established under the new conditions. However, the fronts moved differentially with time depending on the element. In addition, Al was still increasing at the end of the irrigation experiment being the ion that was slowest in response, but of greatest magnitude in response. In contrast, Al in the 75 cm depth was much less mobile regarding treatment showing the immobilization of Al with depth and its dependence on another ion, H. Hydrogen was likewise increasing precipitously even at the end of the 100 cm acid rain treatments, for both the treatments 3.0 pH and 3.7 pH. Hydrogen displayed adsorption plateaus indicating replacement of cation. Thus, some ions were affected directly by the acid rain and some were dependent on other soil chemistry dynamics to occur before mobility was affected. The higher the H concentration the more rapid the maximum response was manifested.

Aluminum was much slower than the other cations in response to the acid treatments. The soil dynamics had to be changed to cause a mobilization. This was a pH response which occurred abruptly, but only at the upper soil surface. At 75 cm there was less response. This indicated the great mobility of Al and its entry into soil solution in large quantities. However, it also showed the great capacity of the soil to immobilize Al and H. Thus, if only the dynamics of soil Al were observed at the soil surface, there would be some concern for detrimental effects. This indeed might be actually true in regard to plant root effects and toxic concentrations. However, when considering the overall effects of acid rain on aquatic systems in proximity to soil, the concern is much less (except for the soil in close proximity to the lake or stream systems which could indeed contribute Al to the water catchments).

In the case of NH_4-N, there was indeed some enhancement in the upper depth. This ion was in low concentration in the rain and showed some increase, probably due to conversion of the NO_3-N and to microbial processes.

Nitrate was very dynamic in the soil showing great mobility, the losses mainly due to plant uptake and microorganisms, conversion to ammonium-N, and accumulation at depth.

The mass ion movements and dynamics of ion mobility appeared to be related to hydrogen. As hydrogen was continually adsorbed in the initial irrigations and column studies, the other cations were leached. Once these cations decreased in quantity on the exchange sites, hydrogen began to increase in soil solution passing the 15 and 75 cm depths, as manifested in lowering soil pH levels, whereby Al finally was mobilized and its concentration increased along with the H. However, these two ions also were immobilized with depth. It is, therefore, likely that at some depth in the soil the effects of these two acid rain treatments would be unobservable. This depth would vary with element, and all equilibrium depths would depend on the quantity of rain and pH of the rain. If the water table were encountered before this equilibrium depth were reached, then there could be horizontal ion effects on aquatic systems as the ions moved into these regimes.

Comparison between two years (which varied in amount of rainfall added) and the background yearly input showed that for some elements, e.g., NO_3-N, Ca, Mg, there were no effects and for others there were yearly differences, e.g., SO_4. Curve shape and within-curve undulations also varied with element but were similar over years. The controls showed little variation. This indicated that the acid treatments had shocked the soil and set in motion very interesting internal adjustments with the soil tending to re-establish equilibrium conditions with time. After 100 cm acid rain, the soil was still adsorbing 66 percent of the ion activity in the input rain. Equilibrium conditions were established in the columns showing that columns can be used to show the dynamics of ion movement and that the Candler soil established equilibrium conditions well before 100 cm acid rain for the 3.0 and 3.7 pH treatments. The same trends for ion mobility occurred for all treatments for both depths, varying only in magnitude and time, and not sequence of ion removal. However, the lower depth showed a modifying effect.

Ion Adsorption

Data for both field and column showed adsorption to be occurring for most of the ions. The major anions added in acid rain were SO_4 and NO_3-N. The SO_4 was greatly adsorbed and affected the movement of the cations as it formed an anion bridge. Indeed, SO_4 was adsorbed increasingly with depth which retarded cation movement and indirectly assisted in alleviating the leaching effects of acid precipitation. A moving front of SO_4 could also be observed with depth The SO_4 at 75 cm depth for 3.0 pH treatment exhibited two adsorption troughs as this ion attempted to establish breakthrough conditions There was an initial adsorption followed by increased amounts in the leachate as the other cations were also being replaced from the soil and entering soil solution As the cations then decreased in concentration in the leachate, the SO_4 also decreased in concentration as adsorption commenced again. As the H and Al then increased dramatically in the leachate, the SO_4 again also increased and finally established breakthrough (i.e., output = input) The adsorption curves for H and SO_4 coincided in shape. Phosphorus was leached by the acid rain with immobilization occurring by 75 cm depth There was an overall decrease in ionic strength with depth. The H and SO_4 adsorption countered the increase in cation concentrations The extents of SO_4 adsorption for field and column at 0-75 cm were similar being 37 and 39 percent for 3.0 and 3.7 pH treatments, respectively. However, there was variation with field versus column for the 3.0 pH treatment at the 0-15 cm depth due to differences in water flow characteristics resulting from dissimilar application systems. However, very similar net adsorptions occurred in the 15-75 cm depth (mean of 3.29 E x 10^3/ha or 158 kg/ha SO_4 or 38 percent of the amount applied in the acid rain). For the 3.7 pH treatment, similar net adsorption occurred in the 0-75 cm depth. The mean net adsorption in the 0-75 cm depth for the 3.0 and 3.7 pH treatments were 49 and 20 percent, respectively of that added in the acid rain.

Nitrate-N showed great variation between field and column. Considering the dynamics of nitrogen under field conditions compared to closed column system, the disagreement between field and column was not surprising. No adsorption of nitrate was observed to occur in the column, but was observed in the field experiment as a considerable loss. As much as 79 percent of that added was lost in the 3.0 pH treatment, probably as uptake to plants and NO_3-N conversion. The corresponding figure for the 3.7 pH treatment was 72 percent. Thus, an average of 75 percent of the N added as NO_3-N was lost (adsorbed, uptaken, or converted). Adsorption was probably minimal. More than 90 percent of the NO_3-N lost was in the 0-15 cm depth.

Hydrogen was highly adsorbed and acted as the major replacing ion in the acid rain soil system, averaging 96 percent adsorption for field and column for 3.0 pH treatment and 88 percent for field and column for 3.7 pH treatment. More than 95 percent of the H was adsorbed by the 0-15 cm depth for both treatments.

Effects on Soil Chemical Properties

Both treatments decreased the pH of the soil solution in the column study. The 3.0 pH treatment decreased the solution pH to below the initial soil pH of 4.87 and at 100 cm rainfall was 4.2 pH. The means for the irrigation period for 3.0, 3.7, and 4.6 pH treatments for 15 cm depth were 4.87, 5.55, and 6.40 pH, respectively. For 75 cm, the means were 5.92, 6.02, and 6.53 pH, respectively. The corresponding figures for the actual field soils for the 15 cm depth were 4.63, 4.83, and

5.00. For the 75 cm depth, the corresponding figures were 4.53, 4.63, and 4.73 pH, respectively. The 3.7 pH treatment decreased the soil pH at 15 and 75 cm by 0.2 and 0.1 pH units, respectively. Corresponding figures for 3.0 pH were 0.4 and 0.2 pH units, respectively.

The cation distribution in the base exchange for Ca, Mg, K, and Na was 53, 30, 11, and 6 percent, respectively, and occupied 4.7 percent of the CEC. The treatments had the greatest effect on the removal of Ca up to 77 percent for 3.0 at 15 cm which also showed the greatest treatment variation. The variation was narrower for Mg with K showing little treatment effect averaging 32 percent loss of the K. Overall reduction for the three ions at 15 cm was for 3.0 and 3.7 and controls were 63, 36, and 21 percent, respectively (discounting ion replacement). For the 75 cm depth, reductions were 37, 18, and 11 percent, respectively. Thus, about twice the amount of cations were lost from the 15 cm than the 75 cm depth. Losses ranged from approximately 2.5 to 0.2 percent of the CEC. The quantitative movement of the ions was also a reflection of their relative concentrations on the exchange sites (i.e., of the base saturation). The 3.0 and 3.7 pH treatments removed the cations in the same order of decreasing dominance as available ions on the exchange sites, i.e., Ca, Mg, K, and Na.

Flow rate had little effect on removal of ions from the Candler soil although there was an overall tendency for a slightly higher removal by the slower flow rate. More significantly, a given flow rate affected each ion differently. Although the rate removal curves were similar in shape, flow rate had no difference on Ca removal, Mg was removed directly with flow rate, and K was removed inversely with flow rate. Obviously each ion must be assessed individually as to leachability under specific conditions

More important than rates of flow were quantities of water applied The lower the quantity applied, the slower the movement of the wetting fronts, thus the less rapid the transport of ions to depth in the soil. Even low quantities of rainfall moved to great depths in the Candler soil and thus also moved the ions to great depth in the soil. Although the magnitude of loss of ions varied directly with the quantity of rain applied, the concentration of ions in soil solution remained the same regardless of the quantity applied.

Concomitant with the ion loss in the soil solution, when the soil itself was analyzed there was a corresponding reduction in the cations present. For the 3.0 pH treatment this was 50 percent cation loss. However, this was also only about 50 percent of the amount lost in the acid rain leachates, which indicated a replenishing of the lost cations by either weathering or input from allocthonous sources. The leachate loss was thus a truer indication of cation loss than was the soil decrease in exchangeable cations. The removed cations from the 0-15 cm depth were adsorbed in the 15-75 cm depth which masked any tendency for a decrease in soil cations due to replacement by H. Thus, ions were removed below the 15 cm depth and increased the base saturation in the 15-75 cm depth, as well as were moved to below 75 cm depth. For the 3.7 pH treatment, the losses in leachate versus reduction the soil were approximately the same. This could preclude input from external sources and attribute the additions to the deficit to mineralization or conclude for the 3.7 pH that the figures were only coincidentally approximately equal.

Actually, other calculations external to the data presented indicated that both are correct and there were external sources added as well as weathering occurring. Net ion losses below 75 cm depth for the 3.0 pH treatment were 0.99 E x 10^3/ha and the 3.7 pH treatment removed 0.32 E x 10^3/ha.

Two-Dimensional Water Flux

Vertical Flux

Movement of irrigation water in the profile and the amount moving to depth and to the water table was found to be dependent on the amount of water applied. This directly affected the total quantity of ions moving to depth and to water bodies nearby. These parameters were established for the conditions at the site and showed that by 48 hours most of the water had moved below 15 and 75 cm depth and to the water table. Thus, sampling of soil leachates, especially at low rainfall amounts, must be integrated over at least a 48 hour period. Flux information on initial (or resident water) conditions, movement of water fronts with time to depth and its quantification, percent of water lost to the water table with time, depth of frontal movement, and rate of frontal movement were clearly established for the rainfall amounts applied in the experiments and for a large event to establish two-dimensional flow in the soil and in the water table. The Candler soil quickly re-established equilibrium moisture conditions with depth after each event, and moisture profiles with depth to the water table showed a stable curve. At 96 hours, equilibrium conditions had been re-established for both the chemistry and flux and the concentration of ions in solution that had been affected by the acid rain had decreased to preirrigation concentrations. Thus, each acid rain event acted as a pulse in the removal of ions and quickly re-established equilibrium conditions. Water content under natural conditions ranged from 2 percent at the soil surface to 12 percent near the water table and was a normal water distribution pattern with depth at the irrigation site.

Each quantity of rainfall had a characteristic series of flow curves with depth and time. The amount of water lost to the water table increased with time. Water loss to the water table occurred immediately upon application to the surface due to miscible displacement. The higher the amount of rainfall, the higher the infiltration rate with corresponding deeper frontal movements. However, regardless of quantity of water applied to the surface, there was a decreasing infiltration rate with depth which was discrete for each amount of rainfall. The irrigation water content in the soil decreased with time and depth as the water front moved downward. The higher the rainfall, the higher the percentage removal of water to the water table. The higher the rainfall, the more rapid the water front moved to the water table. The larger the rainfall, the higher the percentage of irrigation rain that passed respective depths at 48 hours. As much as 55 percent of a 5 cm rainfall moved below 15 cm by 48 hours and 84 percent moved below 75 cm by 48 hours postirrigation. The corresponding figures for 7.5 cm rainfall were 98.6 and 99.7 percent. Even a very large rain event representing about 30 percent of the annual rainfall did not increase the volumetric water content of the Candler soil to above 39 percent of the pore volume showing the great capacity of the Candler soil to conduct water rapidly to great depths. Movement of the front to the water table was rapid at a flow rate of 45 cm/hr at the water table proximity, having reached the water table in only 9 hours after application over a distance of 4 meters. Infiltration rates for 7.5 and 5.0 cm rainfall were 14.2 and 11.7 cm/hr. The lower applied amounts of 7.5 and 5 cm took 27 and 33 hours, respectively, to reach the water table.

A large rain event moved about 1/3 of the resident water into the water table before the irrigation water front itself reached the water table. By 48 hours, 95.6 percent of the irrigated volume of water had moved into the water table. For a very large rain event, approximately 50 percent of the water lost to the water table is resident water.

Horizontal Flux

A direct effect of the irrigated rain was manifested in a fluctuation in the water table as discerned using recorders of water table rise and fall. There was little indication of nonvertical flow. Well recorders used to detect movement of water into the water table and a neutron probe used to follow moving fronts of water vertically in the soil gave data which coincided very well regarding time and quantity of water moving to and into the water table. A transect of wells towards the lake clearly established the magnitude, extent, and time of the water table fluctuations. Water mounding occurred rapidly at the water table. A series of curve shapes were manifested as the mounded water reached equilibrium again with the water table. For even a very large rain event, this equilibrium time was less than 72 hours with 38 percent of the irrigated being detected as mounded water. The height of mounding of the water at the water table was 28 percent (10 cm) of that irrigated on the surface. The water table front moved horizontally, similar to a ripple effect, at a rate of 350 cm/hr which was almost 5 times the gravitational hydraulic conductivity. This was 7 times more rapid than the vertical frontal movements of 43 cm/ha. The water that entered the water table by miscible displacement was detected as a loss before the vertical front reached the water table. It was accounted for by the well recorder at the water table as a gain prior to the vertical water front reaching the water table.

A neutron probe and wall recorders can be used in conjunction to establish two-dimensional patterns and account for losses and gains in each of the respective water regimes.

To calculate the quantities of nutrients passing a given depth in the percolating water, a factor must be applied depending on the amount of rain irrigated onto the soil surface. A table of factors was established relating amounts of water moving past 15 and 75 cm depth to the amount applied at 0 to 48 hours postirrigation. At 15 cm depth, for 1 to 12 cm rainfalls, the factors ranged from 0.93 to 0.99 percent, respectively. For the 75 cm depth, the factors ranged from 0.37 to 0.94 percent, respectively.

Two-Dimensional Ion Movement

The use of soil solution suction cups, water table well recorders and tracers such as iodide were used to discretely establish rates and the extent of ion movements in soil water phases both vertically and horizontally. Complete vertical and horizontal ion profiles were established for each ion. The detail for these profiles depended entirely upon the sampling intervals and analytical effort imposed. Water bodies can be affected in relatively short periods from two-dimensional flow water that has fallen on soil in proximity to these water bodies. Coinciding with the water movement, the concentration of the various ions showed differential movement along the water table similar to the soil profile. Thus, there was a vertical horizontal regime of ion movement. Iodide adequately traced the water front and coincided with the well recorder data verifying the time sequences of water movement. In addition, the observance of a natural ion gradient which increased with proximity to the lake was a measuring indicator of ion movement simply by its dilution with time. Iodide was initially flushed vertically in the soil moving with the water front and being distributed evenly. As the sampling times doubled, the iodide concentration halved showing a rapid geometric decrease in iodide as the soil water drained. The I moved rapidly horizontally in the water table and against an increasing iodide natural gradient near the lake, and gradually decreased over a 14-day period. Potassium, the companion tracer with iodide, moved more slowly but similarly to iodide, both vertically and horizontally, toward the lake 28 m distance. Calcium and magnesium decreased vertically in the soil profile with time. In the water table regime, the zone of increasing concentration became more restricted three-dimensionally for Ca and Mg than K and I. The trend of pH depression with time was observed in the horizontal regime. This indicated that the acid rain was manifested some distance from the site of the rain event and H was carried towards the lake showing maximum affect at 48 hours. Although Ca, Mg, and K and I could be observed in the water table in proximity to the lake, Al was not detected in quantities above background, the Al in the lake being above that along the water table. The electrical conductivity showed an overall increase vertically in ion concentration with a maximum at 48 hours. In the water table regime, there was a concentration front that moved discernibly with time towards the lake. However, the chemical front was delayed compared to the physical water front, moving at a rate of I m/day.

Anions moved rapidly in both the vertical and horizontal phases, moving essentially with the water front. The rate of movement for the cations was lower than for the anions. The zone of movement in the water table in proximity to the irrigated plot was more restricted for the cations than for the anions.

There was a natural ion concentration gradient around the lakes in the study area. This gradient increased with increasing proximity to the lake edge, the well nearest the lake (about 3 m distence) having the highest concentration of ions. The ion concentrations in the lake water were also lower than in the near-lake region. Thus a series of concentric rings could be drawn around the lake showing decreasing ion concentration with distance from the lake. Thus nutrient supply to the lake via the water table would be generally negligible when considering the flushing effect of the gradient. However, movement of Al in the soil leachate in close proximity to lake systems could be potentially a hazard and a source of seeding of lakes with Al from the surrounding soil. The gradient was no doubt an evaporation artifact of the lowered water table in the region over the past years. Indeed, in periods of a rising water table, the gradient would be much decreased, and a more direct effect of the horizontal movement of ions in the water table towards the lake would be expected.

Ion Net Losses and Mass Balances

Ions were lost from the soil with each and every rainfall event. The net losses of cations and anions for the field and column studies showed similar trends regarding the magnitude and relative losses among ions. Although greater ion movements were noted in the field experiments due to natural ambient conditions and the effects of cumulative events, the net ion movements for field and column studies were similar for treatment and depth. Each ion was different regarding magnitudes of losses.

Field net losses for cations and anions for 3.0 pH treatment at 15 cm depth for Ca, Mg, Al, Na, H, K, SO_4, Cal, NO_3-N, and P were 49, 10, 14, 2, 0.01, 0, 254, 9, 6, and 0 kg/ha, respectively, for a total of 343 kg/ha (10.9 E x 10^3/ha). For the 3.7 pH treatment at 15 cm, the corresponding net losses were 11, 3, 1, 1, 0, 0, 43, 4, and 0 kg/ha, respectively, for a total of 60 kg/ha (1.9 E x 10^3/ha). For the 75 cm depth, corresponding figures for the 3.0 pH treatment were 20, 8, 0.1, 3, .01, 0, 101, 22, 3, and 0 kg/ha, respectively, for a total of 155 kg/ha (4.6 E x 10^3/ha). For the 3.7 treatment, the corresponding figures were 12, 2, 0.1, 0.7, 0.01, 0, 40, 0, and 0 kg/ha, respectively, for a total of 55 kg/ha (1.5 E x 10^3/ha). The magnitudes of cation losses for the field experiment for the both depths and treatments 3.0 and 3.7 pH were thus as high as 50 kg/ha and for the anions as high as 254 kg/ha. Corresponding figures for the column study were 55 kg/ha and 338 kg/ha. The net loss of ions from the 3.0 pH treatment was thus considerably higher than for the 3.7 pH treatment. The order of decreasing loss for the three nutrient cations was Ca>Mg>K for both field and lab studies for both treatments and both depths. This order of net loss was in proportion to their availability on the exchange sites. Essentially no net K was lost due to treatment effect. Calcium was the cation showing greatest net loss.

The field experiment showed more sulfate adsorption than the column experiment for both depths and both treatments. This could be explained by the nature of the pulsed rain for the field applications compared to the continuous column applications. However, the proportions adsorbed were similar for field and column experiments. Both field and column experiments showed that more than 50 percent of the SO_4 was adsorbed by 75 cm from the 15 cm depths for both treatments at both depths.

Nitrate showed great variation when comparing field and column. Much more NO_3-N was adsorbed or lost in the field than in the columns which could readily be explained by plant uptake and microbial conversion processes in the field. Indeed, such differences would be expected when compared to the input N concentrations. Ammonium-N showed elevated losses above that added in the rain in the field. Obviously, the excess NH_4-N was the result of conversion of the NO_3-N by microorganisms and adding both forms of N much more closely approximated the N added in the rain solely as NO_3-N.

Most of the added H was adsorbed for both experiments treatments and for both depths. Since the H was the major ion added in the system, it obviously played a major role in the exchange processes internally in the soil. More than 92 percent of the added H was adsorbed, the mean over depth and treatment being 95.4 percent. Hydrogen adsorption accounted very well for the sum of the replaced cations. Any imbalance that occurred for both treatments at 75 cm depth could be accounted for by the quantity of Al immobilized in the 15-75 cm depth. Very little H was thus lost or adsorbed in nonexchange reactions such as adsorption by the organic matter phase.

Aluminum was mobile in the Candler soil. Both field and column experiments recorded losses even in the controls. A high percentage of the Al (more than 55 percent) that passed the 15 cm depth was adsorbed by the 75 cm depth for both treatments for both experiments. Thus, although Al showed great mobility with depth, the Candler showed a great capacity to immobilize the Al with depth. The treatments 3.7 and 3.0 pH removed past 15 cm approximately 4.5 and 20 times, respectively, that moved past 15 cm by the control treatment. Similar figures for the 75 cm depth were 1.5 and 15 times the control. Although the loss of Al was quantitatively substantial, being as much as 58 kg/ha, this represented less than 7 percent of the cation exchange capacity which was 95 percent Al-saturated. Substantial quantities of Al also moved past the 75 cm depth. However, only in the 3.0 pH treatment at 15 cm depth was the concentration of Al in soil solution above 0.2 mg/L and which could be toxic to plant roots. Net losses of Al at 15 cm depth for 3.0 and 3.7 pH treatments were 54.9 kg/ha and 10.4 kg/ha, respectively. Corresponding net losses for 75 cm depth were 24.6 and 0.9 kg/ha, respectively.

Mass balance data showed good agreement in the cation-anion balance and that the analysis was of high quality. There was only a 1.8 percent difference between the sum of cations and anions for the two treatments at the two depths. The mass balance data also showed that the column and field experiments compared well which was one of the hypotheses for the study. Mass balance data agreed better for the 3.7 than the 3.0 pH treatments.

On a quantitative net basis (treatment minus control), the 3.0 pH treatment removed a total of 408 kg/ha (14.6 E x 10^3/ha) of ions below the 15 cm depth and 242 kg/ha (8.7 E x 10^3/ha) below the 75 cm depth. This showed the magnitude of ion loss and also 41 percent adsorption with depth. The corresponding figures for the 3.7 treatment were 77 kg/ha (3.2 E x 10^3/ha) and 69 kg/ha (2.3 E x 10^3/ha), respectively, for a 10 percent adsorption.

Generally, laboratory column studies can closely approximate field studies. Due to the variability in response to the ions, no one treatment, application rate, or quantity applied will correlate well for all ions for both field and column studies. Degree of agreement between field and column studies is dependent on many factors, not the least being amount of rainfall applied, the natural ambient rainfall for the period on the field site, and the depth of soil being compared.

Field losses of ions compared well with the 15 cm depth in the column studies under low application. Higher field applications of acid rain agreed better with the 75 cm depth in the column study

Agreement in ion losses were within 88 percent for both conditions Thus the study of movement of ions by laboratory soil columns compared well with field studies and viable conclusions can be drawn about field soil losses of nutrients by laboratory soil columns.

For the 3.7 pH treatment, the data for the lower amount of rainfall (1981) showed a net ion loss of 88 percent of the column data for the 15 cm depth This compared with 55 percent for 1982 under larger rainfall amounts At the 75 cm depth, the larger amount of rainfall (1982) agreed better with the column ion loss, being 88 percent of the column loss Thus the dynamics of water flow under field conditions will affect the correlation with laboratory studies It is apparently much more critical to standardize column conditions to field conditions for application rate, pulsed amounts, etc., for short surface columns However, pulsing rain under unsaturated conditions in the laboratory would be extremely time-consuming and would defeat the concept of approximating field conditions by laboratory studies using a simplified rapid method.

APPENDIX I
TOTAL DYNAMIC HEAD

TDH = H_p + H_{fm} + .76 H_{f1123} + H_e + H_s

where H_p = pressure head

H_{fm} = main line friction head

H_{f1123} = lateral line friction head, 3-part

H_e = elevation head

H_s = suction head or lift

H_p @ 38 psi

Head in feet = pounds psi x 2.31 psi
= 38 x 2.31 psi/ft-psi
= 87.8 ft

H_{fm} rate = 24 gpm (from 12 sprinklers @ 2.2 gpm @ 38 psi)
mainline length will be 300 ft, 1½ dia. pipe 3 mainlines

1--from pump to first lateral = 40' @ 25 gpm
2--from 1st lateral to 2nd lateral = 120' @ 16 gpm
3--from 2nd lateral to 3rd lateral = 120' @ 8 gpm

H_{fm1} = 3 (1 psi/100 ft (tables) x 0.4 x 2.31) = 2.76'

H_{fm2} = 3 (0.41 x 1.2 x 2.31) = 3.42'

H_{fm3} = 3 (0.13 x 1.2 x 2.31) = 1.08'

H_{fm123} = 7.26 ft

H_{f1123} Three laterals @ 8 gpm, 1 lateral per plot

1--from mainline to 1st sprinkler = 40' @ 8 gpm, 1"
2--from 1st sprinkler to center plot = 20' @ 6 gpm, ½"
3--from center plot to 3 sprinklers = 3 x 20 @ gpm, ½"

H_{f11} = 3 (0.84 x 0.4 x 2.31) = 2.34'

H_{f12} = 3 (5.8 x 0.2 x 2.31) = 8.04'

H_{f13} = 3 (1 x 0.6 x 2.31) = 4.17'

H_{f123} = 2.34' + 8.04' + 4.17' = 14.6'

H_e - vertical rise - 41.5'

H_s = suction head or lift below pump to pump

If 30 ft from lake, the rise is about 5' from the lake surface to the pump 2" pipe PVC, 24 gpm

H_s - 5' + (0.36 x 2.31 x 0.3 = 5') + .25' = 5.25'

TDH - 87.8' + 7.26' + 0.75 (14.6') + 41.5' + 5.25' = 152.8' of head

There are some friction losses through the various valves, gauges, meters, elbows, etc. Estimated to be 1 psi or 2.31' of head

TDH = 152.8 + 2.3 = 155.1'

From the graph of efficiency provided with the pump, this pump will supply ample TDH and thus gpm to push the system, i.e., at slightly higher psi (38-40) than in the calculations for the first pump, the pump will supply 150 gpm full throttle. We require only 24 gpm, so are operating at far less than full throttle.

Note. When the Chemilizer is in operation for the acid rain irrigation, extra TDH loss occurs to push the dilution system of that instrument

APPENDIX II
PUMP EFFICIENCY

BRAKE HORSEPOWER (BHP) = $\frac{\text{TOTAL DYNAMIC HEAD x GPM}}{\text{3960 x EFFICIENCY}}$

EFFICIENCY = $\frac{\text{TDH x GPM}}{\text{3960 x HP}}$

For the model XLS2-19, Eff. = $\frac{160' \times 50 \text{ gpm}}{3960 \times 4.5 \text{ BHP}} = \frac{8000}{17820} = 0.45$ (45%)

i.e., at 160' head, the pump should evacuate 50 gpm. Under field conditions, max. output full throttle was 19 gpm. The design called for 24 gpm. Eff. only 16%.

Conclusion. Pump could not operate at its specifications nor under specified field operations.

For model FP-250, Eff. = $\frac{160' \times 140 \text{ gpm}}{3960 \times 10 \text{ BHP}} = \frac{22400}{39600} = 0.57$ (57%)

This larger pump was rated at 270' TDH. The additional head allowed for an increase in pressure on the lines from 30 psi to 38 psi. Pump at discharge had a pressure of 55 psi, and operated at about 2/3 throttle, putting out 24 gpm very steadily per transect in 1981

This pump was not tested for maximum pumping rate for fear of some damage or dislocation of lines under high pressures

In 1982, the pump irrigated all three transects (9 plots) simultaneously at a rate of 75 gpm (½ capacity) at 2/3 throttle

APPENDIX III
HYDROGEN IN THE SIMULATED ACID RAIN

A. pH REGIMES IN THE SYSTEM

1. pH of Lake McCloud = 4.7 = pH or irrigation water since the lake is source of control rain

   pH of acid rain = 3.7 = pH of simulated rainfall imposed on the field plots (1981)

   3.0 = pH of simulated rainfall (1982 and 1981)

   pH = -log H ion concentration

   pH = 3.0 = 0.001 g H^+/L - 1000 μeq/L

   pH = 3.7 = 0.0001995 g H^+/L = 199.5 μeq/L

   pH = 4.7 = 0.00001995 g H^+/L = 19.95 μeq/L

2. Volume-weighted pH of the total water on the plots

   averate precipitation as natural rainfall = 56" on Lake McCloud acidified rainfall is to be added by irrigation at the following rate

   1981--2½"/week, 2 weeks per period, 4 periods per year,
   pH 3.7 = 20 inches

   1982--4"/week, 2 weeks per period, 4 periods per year,
   pH 3.7 and pH 3.0 = 32 inches

   a) pH 3.7, 16" irrigated simulated acid rain:

   Total water on the plots areas = 56" (annual natural rainfall)
   16" (artificial imposed)
   72" (natural + irrigated)

   The volume weighted pH of the anticipated 72" of rainfall is

   let X = 16" of H loading
   let 3.5X - normal loading of H^+, i.e., 56/16

$$\begin{aligned}\text{Total } H^+ \text{ loading} &= \text{acid } H^+ + \text{normal } H^+\\ &= X + 3.5X\\ 4.5X &= 0.0001995 \text{ g } H^+/L + 3.5\ (0.00001995) \text{ g } H^+/L\\ 4.5X &= 0.0002692 \text{ g H/L}\\ X &= 0.0002692/4.5\\ X &= 0.0000598 \text{ g H/L}\\ X &= 59.8\ \mu\text{eq/L}\\ pH &= 4.22\end{aligned}$$

The equivalent loading that would result in the present volume if rainfall annually on 56" basis not 72" basis would yield a weighted pH of

$$\begin{aligned}3.5X &= 0.0002692 \text{ g H/L (as above)}\\ X &= 0.0000769 \text{ g H/L}\\ X &= 76.9\ \mu\text{eq/L}\\ pH &= 4.11\end{aligned}$$

b) pH 3.7, 32" irrigated simulated acid rain.

Total water on the plots areas = 56" (annual rain normal)
32" (artificial imposed)
88" (natural + irrigated)

The volume weighted pH of the anticipated 88" of rainfall is

let X = 32" = H loading from acid rain
let 1.75X = H loading from control rain = 56"

$$\begin{aligned}\text{Total H loading} &= \text{acid H} + \text{normal H}\\ &= X + 1.75X\\ &= 2.75X\\ 2.75X &= 0.0001995 + 1.75\ (0.00001995)\\ 2.75X &= 0.0002343\\ X &= 0.0000852\\ pH &= 4.07\end{aligned}$$

The equivalent loading if the total H loading was occurring in the 56", i.e., with the normal rain, is

$$\begin{aligned}1.75X &= 0.0002343\\ X &= 0.00013389\\ pH &= 3.87\end{aligned}$$

c) pH 3.0, 32" irrigated simulated acid rain.

Total water on plots areas = 88"

Total H loading = 2.75X if in 88" or 1.75X if in 56"

2.75X = 0.001 + 0.00001995 (1.75)
2.75X = 0.0010348
X = 0.0003763
pH = 3.42

1.75X = 0.0010348
X = 0.0005913
pH = 3.23

8. ADDING ACID TO THE SYSTEM

1. pH 3.7 and pH 3.0 vs g H/L

a) pH 3.0 = 0.001 g H/L = 1000 µeq/L

b) pH 3.7 = 0.0001995 g H/L = 199.5 µeq/L

c) pH 4.7 = 0.00001995 g H/L = 19.95 µeq/L

Since the added lake water is already at pH 4.7, the difference added artificially will be (in g H/L)

b-c = 0.0001796 for pH 3.7 = 179.6 µeq/L
a-c = 0.0009801 for pH 3.0 = 980.1 µeq/L

i.e., if one adds 0.0001796 g H (or 0.1796 mg H) per liter of lake water at pH 4.7, the resultant pH will be 3.7 which is the simulated acid rain desired for the irrigation. Similarly for 3.0, adding 0.9801 mg H/L will result in a pH of 3.0.

2. Stock solution concentrations

Ratio of H_2SO_4 and HNO_3 to add. To simulate throughfall chemistry the acids used for simulated acid rainfall are sulfuric and nitric acid in a ratio of 7:3 (v/v).

3. Normality of concentrate stock

Normality of nitric acid = sp. Gravity x 1000 x %conc./eq.wt x 100
= 1.42 x 1000 x 70/64 x 100
= 15.8

Normality of sulfuric acid = 1.84 x 1000 x 96/49 x 100
= 36.05

Normality of mixed stock of these acids:
(.70 x 36) + (.30 x 15.8)/100 = 30.01

i.e., 1 L of 70:30 H_2SO_4:HNO_3 @ 30 N contains 30 g H

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4. Intermediate stock solution for acid rain irrigations

From the 0.1796 mg/L of water at pH 4.7 to yield a pH of 3.7: the sulfuric acid contributes 0.1796 x .70 = 0.1257 mg H/L. The nitric acid contributes 0.1796 x 0.30 = 0.0539 mg H/L.

Thus by diluting the concentrated acid stock solution of 30 N by a factor of 30 g/0.0001796 g, the resultant solution will contain 0.1796 mg H/L = pH 3.7. The factor is 167,000. This is a very large dilution factor and must be made stepwise, i.e., 1 to 167, then 1 to 1000.

Similarly, the same approach can be used for the pH 3.0 irrigation. The sulfuric acid contributes:

0.9801 x 0.70 = 0.6861 mg H/L and the nitric acid contributes
0.9801 x 0.30 = 0.2940 mg H/L

The dilution factor is 30/0.0009801 = 30,600. This is also a very large factor and must be made stepwise, i.e., 1 to 30.6, then 1 to 1000.

Preparing the intermediate acid solution for the Chemilizer

6. Time of irrigation

4 sprinklers @ 45 psi = 2.2 gpm/sprinkler
for 12 sprinklers = 2.2 x 12 = 26 gpm

At a rate of 26 gpm, it will take 1508/26 = 58 minutes to irrigate the transect (three plots) with 1" rain, for 2", it will take 58 x 2 = 116 minutes (1 hr, 57 minutes).

It was subsequently decided to operate the pump at a higher gpm to irrigate two transects in the same time period. This required a rate of 26 x 2 = 52 gpm. The pump was moved closer to the lake and could easily do this operation.

The irrigation per hour was thus 1508 x 2 = 3016 gallons on the two transects at the rate of 1" per hour. For a 2" event, it thus took two hours approximately and total gallonage imposed was 3016 x 2 = 6032 gallons.

It was then subsequently decided that the three transects would be irrigated in one operation. The pump would operate at about 3/4 throttle at a psi at the pump head of 65 psi. The pressure at the sprinklers was 40 psi on all plots. Thus an hourly rate of 3 x 26 = 78 gpm and a total of 4524 gallons per hour or 9048 gallons in approximately 2 hours for a rate of 1" per hour or 2" total rainfall for the two hours over the plots.

6 Total amounts (ounces) of intermediate solution applied per irrigation

At 3.3 opm = 191.4 ounces total for 58 minutes, i.e., 191.4/128 = 1.50 gallons. This means that each irrigation of 1" over each transect (three plots) will use 1.5 gallons of the intermediate solution in the Chemilizer. For two hours irrigation, each Chemilizer will use 3.0 gallons to maintain the pH of 3.7 on the transect, but note that the concentration for this transect will be higher correspondingly. Make up 4 gallons each time an event is imposed on the transect.

7 Amount of conc. 70:30 acid mix to add per irrigation

The intermediate solution is itself a dilution from the concentrated acid mix, i.e., the 1.5 gallons is diluted by a factor of 167 for the 3.7 rain and by 30 for the 3.0 rain.

1.5 gal (191.4 oz)/167 = 1.146 oz or 1.146 x 29.6 = 34.0 mL
1.5 gal (191.4 oz)/30.6 = 6.25 oz or 6.25 x 29.6 = 186 mL

For the two hour irrigation for 2" acid rain, it will thus take

34.0 x 2 = 68.0 mL concentrate diluted to 3 gallons for pH 3.7
186 x 2 = 370 mL concentrate diluted to 3 gallons for pH 3.0

However, to make them up in oversupply for the Chemilizer bag, for a total volume each irrigation in the Chemilizers of 4 gallons.

86.0 x 4/3 - 90.6 mL for the pH 3.7 transect
370 x 4/3 - 494 mL for the pH 3.0 transect
167/30.5 = 5.46

pH 3.7 = 0.0001995 g H/L - 0.00001995 g H/L = 0.0001796 g H/L
pH 3.0 = 0.0010000 g H/L - 0.00001995 g H/L = 0.0009801 g H/L
0.0009801/0.0001796 = 5.46
34.0 - 5.46 = 185

Thus for the Chemilizer irrigating the 3.7 transect,

ADD 91 mL of CONCENTRATE ACID MIX AND MAKE TO 4 GALLONS,

and for the Chemilizer irrigating the 3.0 transect,

ADD 494 mL of CONCENTRATE ACID MIX AND MAKE TO 4 GALLONS.

8 pH of the intermediate solutions

i.e., the first dilution pH of intermediate solution after 1st dilution (1 to 167) for 3.7 is log 0.1796 g H/L = 0.74 pH The true pH will be higher than this due to suppressed H ion activity at this high concentration. Similarly, the pH of the 1st dilution for 3.0 is

log 0.9801 - 0.01, i e., still very concentrated.

Thus if one dilutes the stock acid by 167 times, the pH will be 0.74. If diluted 30 times, the pH will be 0.01.

These two dilutions are best made on site using a graduated cylinder, lake water as the diluent, and a 5 gallon carboy marked at each gallon level and calibrated for accuracy.

B. pH of the final dilutions using a chemical feed diluter

The intermediate solutions are best diluted using an on-line diluter with controls for the final 1 to 1000 solution.

for pH 3.0. 0.1796 g H/L/1000 = 0.0001796 g H/L (pH 3.76)
for pH 3.7. 0.9601 g H/L/1000 - 0.0009801 g H/L (pH 3.01)

C. THE CHEMICAL DILUTER (CHEMILIZER) SYSTEM

The second dilution of 1 to 1000 is itself accomplished by a stepwise dilution. Since the controls are in English units (ounces and gallons) we will revert to these units for convenience in the following calculations

When metering the intermediate acid solution into the Chemilizer, it is critical to know the flow rate in gallons/minute (gpm). This is first established before the metering device is activated to dispense the acid solution.

A rate of 26 gpm was optimum for irrigating three plots. The acid solution is first metered into 1.5 gpm which is the rate of flow established through the Chemilizer. This is accomplished by downturning the mainline gatevalve to force the mainline water through the bypass Chemilizer at a rate of 1.5 gpm, leaving 24.5 gpm in the mainline flow. The acid control is adjusted to 3.3 ounces per minute (opm) after the 1.5 gpm, bypass water reading is stabilized. The exit from the bypass then allows the acidified lake water to enter the mainline and be further diluted as it enters the system to resume the 26 gpm rate of flow

Factor = 3.3 to 1.5 gallons (192 oz), 1.5 to 26 gallons (3328 oz). Total factor = 3328/3.3 = 1008, which is very close to the factor of 1000 which we require.

I. The pH changes in the stepdown dilutions

3.3 to 192 oz = 58 factor. Thus the pH of the first dilution in the Chemilizer is 0.1796/58 - 0.003097 = pH 2.51 for the pH 3.7

water. Similarly, for the 3.0 final solution water, the pH of the first dilution in the Chemilizer is 0.9801/58 - 0.016898 - pH 1.77.

The final dilution is 1.5 to 26 gpm = 17.33 factor. Thus the two pH waters are further diluted as 0.003097/17.33 - 0.0001787 = pH 3.75. Similarly, for the pH 3.0 line, the pH = 0.016898/17.33 = 0.0009751 = pH 3.01.

Expressed as above an in 2.6, these pHs are not the desired final degree af acid concentration. This is because the acid concentration from the lake water itself is not included since it is background. When including these, as in the true system, the pH final levels are

for pH 3.7. 0.0001787 + 0.00001995 - 0.0001986 = pH 3.702
for pH 3.0. 0.000975 + 0.00001995 - 0.000995 = pH 3.002

These are the final pH readings of the mainline irrigation solutions.

2. pH check on dilutions from the calculations

For pH 3.7

a) Prepare a solution of 70:30 sulfuric:nitric acid. Mix well.

b) Dilute 3 mL of 1 to 500 mL with deionized water. Mix well. Read pH. Calculated pH = 0.75. Determined ________.

c) Dilute solution in 2 using 4 mL to 250 mL in graduated cylinder. Mix well. Calculated pH - 2.51. Found ________

d) Dilute 5.77 mL af solution in 3 to 100 mL in vol. flask, with DW. Mix well. Calculated pH = 3.70. Determined pH = ________.

For pH 3.0.

a) Use prepared acid concentrate as 1 above.

b) Dilute 16.33 mL of 1 to 500 mL with deionized water. Do not read pH

c) Dilute 4.31 mL af this intermediate solution from 2 to 250 mL. Mix Well. Calculated pH = 1.77. Determined ________

d) Dilute 5.77 mL of this solution in 3 to 100 mL. Mix well. Calculated pH - 3.00. Determined ________.

Factors for above $= \frac{500}{3} \times \frac{250}{4.31} \times \frac{100}{5.77} = 167{,}500$ = factor for 3.7 pH

$= \frac{500}{16.33} \times \frac{250}{4.31} \times \frac{100}{5.77} = 30{,}780$ = factor for 3.0 pH

APPENDIX IV

SULFATE AND NITRATE IN THE SIMULATED ACID RAIN

1. pH 3.0

Sulfate: $\frac{36\ N \times 0.7}{30600} = 0.000824\ N$

i.e., 0.000824 N x 48 g/L = 0.0395 g/L = 38.5 mg/L

$$\begin{array}{rr} \text{in lake} = & 7.3\ \text{mg/L} \\ \hline & 46.8\ \text{mg/L} \end{array}$$

or 46.8 x 10 093 = 472.4 kg/ha

Nitrate: $\frac{15.8 \times 0.3}{30600} = 0.0001548\ N$

i.e., 0.0001548 x 14 g N/L = 0.00217 g/L = 2.17 mg/L NO_3-N

$$\begin{array}{rr} \text{in lake} = & 0.16\ \text{mg/L}\ NO_3\text{-N} \\ \hline & 2.33\ \text{mg/L}\ NO_3\text{-N} \end{array}$$

or 2.33 x 10.083 = 23.53 kg/ha (NO_3-N) = 104.2 kg/ha NO_3

2. pH 3.7

Sulfate: $\frac{36\ N \times 0.7}{167{,}000} = 0.0001508\ N$

i.e., 0.0001508 x 48 = 0.0072384 g/L = 7.24 mg/L

$$\begin{array}{rr} \text{in lake} = & 7.3\ \text{mg/L} \\ \hline & 14.54\ \text{mg/L} = 148.8\ \text{kg/ha} \end{array}$$

Nitrate: $\frac{15.8 \times 0.3}{167{,}000} = 0.0000284\ N$

i.e., 0.0000284 x 14 - 0.0003974 g/L = 0.397 mg/L

$$\begin{array}{rr} \text{in lake} = & 0.14\ \text{mg/L} \\ \hline & 0.537\ \text{mg/L} \end{array}$$

or 5.42 kg/ha NO_3-N or 24.06 kg NO_3/ha

3 pH 4.55 (Control)

The Lake McCloud water was used as the water irrigation source for the field experiments. The lake contained 7.3 mg/L SO_4 and 0.14 mg/L NO_3-N (0.62 mg/L NO_3). So the natural ratio in the water is 7.3:0.62 SO_4:NO_3 = 92% SO_4 8% NO_3.

Although the ambient rain falling in central Florida is 70% 25%, 5% of SO_4 NO_3 Cl (w/w), this rain, if falling on a forest ecosystem, will filter through the canopy before reaching the soil. The project was to establish the effect of acid rain on a full canopy natural forested ecosystem, so it was obvious that throughfall rain would be effecting the soil, not the natural rain itself. In addition, the lake water contained other ions in elevated concentrations compared with normal ambient rain. The SO_4:NO_3 in throughfall was about 4.5:1 (or 82:18) (as opposed to 7:2.5 (or 74:26) for ambient rain). The lake water was still wider than this (92:8), but the treatments 3.7 and 3.0 were adjusted close to the 4.5:1 using H_2SO_4 and HNO_3. Using these acids in the 70:30 (v:v) ratio coincidentally accomplished this.

From previous, for 3.0 pH: SO_4:NO_3 = 47.4:104.2 = 92% 18%

for 3.7 pH: SO_4:NO_3 = 246.8:24.1 = 86% 14%

However, the average pH for 1992 for the 17 irrigations for the 3.0 treatment was 3.05, and for the 3.7 treatment was 3.75. This seemingly small difference from the theoretically imposed acid caused a slight adjustment in the absolute quantities of SO_4 and NO_3 applied to the soil for the irrigation period.

From previous pH calculations, which included the H in the lake water pH 4.55 (19.95 µeq/L), the factor for the 3.05 and 3.75 treatments (stepdown by the Chemilizer injectors) was actually 35,253 and

187,852. When substituting these factors in the above calculations, sulfate at 3.06 pH treatment = 420.0 kg/ha and NO_3 at 3.06 pH = 90.3 (472.4 and 104.2 theoretically from 3.00 previous). The SO_4 and NO_3 for the 3.75 pH treatment = 138.7 and 22.1 kg/ha, respectively (14.8 and 24.2 from 3.70 previously). So, although the same percentages apply, the quantity added decreased. It was important to establish these added quantities of losses by adsorption or conversion are to be estimated.

Table IV.1 SO_4 and NO_3 added to plots (kg/ha).

	Treatment		
	3.0	3.7	4.65 (control)
Parameter Applied			
SO_4	420.0	138.7	73.7
NO_3 (NO_3-N)	90.3 (20.4)	22.1 (5.0)	6.3 (1.42)
Parameter Found (Recovery)			
SO_4	417.9 (99.6%)	147.3 (106%)	75.6 (102%)
NO_3	92.0 (101%)	19.2 (87%)	6.7 (106%)

$\bar{x}$ Recovery (%) SO_4 = 102.5%

NO_3 = 98.0%

(factor for mg/L to kg/ha for 100 cm rain)

$$mg \times 75{,}700 \times 133.33 \times 10^{-6}\ kg/mg = 10.093$$

APPENDIX V
ACID DILUTER SYSTEM

A 1:1000 dilution is required to inject 0.0001796 g H^+/L into the system for irrigating at a pH of 3.7 in the simulated acid rain. The "chemilizer" diluter has two settings for solution control. Inflow water from the mainline can be adjusted in the range of 0 to 6 gpm. Injector acid water flow can be adjusted in the range of 0 to 6 oz/min (opm).

Mainline gpm = 24 gpm or 24 x 128_3 = 3072 opm

therefore a rate of 3072/1000 3072 opm =

3.072 ounces per 24 gallons =

1:1000

3.072 is midrange on the acid inflow line, 3 gpm is midrange on the water inflow line.

Thus reduce the mainline gpm to 21 from 24, leaving 3 gpm to flow through the inflow line in the injector which will bypass the injector line and pick up 3.07 ounces of acid solution, thence to exit into the mainline and increase flow rate to 24 gpm.

At this rate of 3.1 oz/min = 186 oz/hr or 186 x 1.06 = 197 oz will be used for the 1520 gallons required for irrigation (1") on the transect. Thus a 4 gallon tank will adequately contain the 197 oz

(197/128 = 1.54 gallons US) required for each inch irrigation (198) for a supply for 2 inches (1982) The ratio of acid solution lake water after injection in the diluter and premixing in the mainline is 3.07 384 = 1:125

APPENDIX VI
COEFFICIENT OF UNIFORMITY FOR PLOT IMPACT SPRINKLERS

Two trials were run on a temporary assembly of the sprinkler-piping system for one plot actual size.

Source of water was an outside tap at the soil science greenhouses at the University of Florida. Pressure was not regulated to 30 psi. Sprinklers were set uniformly and to a radius of about 5 feet beyond the adjacent sprinkler. Radius of 33 ft with distance between sprinklers @ 28.4 ft on the square, 4 sprinklers per plot.

Beakers were set out in a concentric square pattern along the pipe and in the four quadrants, 600 mL beakers were used. Irrigation time was about 40 minutes each time. Measurement was made using a graduated cylinder reading in mL. All nine field plots were subsequently checked periodically and adjustments made to retain a high CU.

Table VI.1. Coefficient of uniformity for plot impact sprinklers.

Trial 1		Trial 2	
mL/beaker (x)	$x - \bar{x}$	mL/beaker (x)	$x - \bar{x}$
61	6	49	3
60	6	43	3
62	7	45	1
63	8	45	1
55	0	45	1
55	0	55	9
58	3	54	8
60	5	46	0
62	7	32	14
56	1	55	9
33	22	34	12
57	2	43	3
29	26	55	9
741	92	601	73
n = 13		13	
$\bar{x}$ = 55		46	
CU = 100 (1-92/711) = 100 (1- 129) = 100 (.871) = 87%		CU = 100 (1-73/601) = 100 (1-.121) = 100 (.88) = 88%	

A reading above 80% is very satisfactory.

APPENDIX VII
PORE VOLUME AND DISPERSION USING TRITIUM

The columns in each set for the two depths were very uniform in dispersion. Thus any differences in the chemistry of the filtrates among treatments can be attributed to treatment effects.

The intercept at midslope in the curve established the pore volume for the column. This coincided very closely with the calculated pore volume determined gravimetrically. The pore volume of the 15 cm and 75 cm columns averaged 292 and 1410 mL, respectively. This indicated little change in pore volume with depth This would be expected since the Candler is a medium sand uniformly to considerable depth.

Since the breakthrough curves obtained from these experiments fit the Brenner solution for convective-dispersive transport, it was assumed that no channeling had occurred in the columns. If this were true, then physical properties were assumed to be similar and therefore chemical comparisons could be made more confidently.

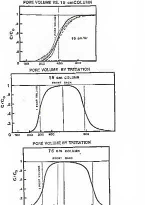

Figure VII.1. Pore volume and dispersion in a column soil using tritium.

APPENDIX VIII
CHEMICAL AND PHYSICAL CHARACTERISTICS OF THE CANDLER SOIL

Table VIII 1. Chemical and physical characteristics of the Candler soil.

	Depth cm	Plot Distance from Lake (m)					
		40		80	120		$\bar{x}$
Cation Exchange Capacity (me/100 g)	0-7.5 0-15 15-75	4.15 3.48 2.34		4.31 3.34 2.10	4.18 3.51 2.01		4.21 3.44 2.15
Extractable Acidity (me/100 g)	0-7.5 0-15 15-30	4.05 3.40 2.30		4.17 3.20 2.01	3.98 3.36 1.93		4.07 3.32 2.08
Base Saturation (%)	0-7.5 0-15 15-75	2.41 2.30 1.71		3.25 4.19 4.29	4.78 4.27 3.98		3.48 3.73 3.53
		Ca	Mg	K	Na	H	Al
Percent of CEC	0-7.5 0-15 15-75	2.04 1.83 1.53	.55 .78 .79	.31 .29 .14	.48 .67 .79	.02 .02 .03	96.6 96.5 96.7
		14 Å Interlayered			Kaolinite		Quartz
		%					
Clay Fraction Analysis	0-15 15-75	38 48			35 27		27 25
Bulk Density	0-15 0-75	1.41 cm^3/cm^3 1.41 cm^3/cm^3					
Saturated Hydraulic Conductivity	0-15 0-75	1.25 cm/min 1.25 cm/min			74.2 cm/hr 74.7 cm/hr		
pH	0-15 15-75	4.8 4.60					
Organic Matter (%)	0-15 15-75	0.75 0.62					

Table VIII.2. Particle size distribution and textural analysis of a Candler Typic Quartzipsamment.

	Particle size distribution (%)								
	Sand						Silt	Clay	
Depth (cm)	VC (2-1)	C (1-.5)	M (.5-.25)	F (.25-.1)	VF (.1-.05)	Total (2-.05)	Total (.05-.002)	Total (<.002)	Textural Class
	mm								
0-15	0.1	3.4	49.6	39.2	2.7	95.0	2.8	2.4	S
30-45	0.0	3.3	51.5	39.3	2.2	96.3	1.4	2.3	S
60-75	0.0	3.4	53.3	37.8	1.9	96.4	1.6	2.0	S
90-105	0.0	4.4	52.4	37.6	2.0	96.4	1.6	2.0	S
120-135	0.0	4.3	52.4	37.8	2.0	96.5	1.7	1.8	S
150-165	0.1	5.4	53.0	37.8	1.6	97.9	0.9	1.2	S
180-195	0.1	5.9	54.1	36.9	1.2	98.2	0.7	1.1	S
210-225	0.1	5.6	50.7	39.5	1.5	97.4	0.0	2.6	S
240-255	0.0	4.6	52.4	36.2	1.7	94.9	0.4	4.7	S
270-285	0.0	5.1	56.0	30.4	1.4	92.9	0.5	6.8	S
300-315	0.1	4.5	56.1	33.1	1.2	95.0	0.7	4.3	S
330-345	0.0	4.6	55.5	33.3	1.3	94.7	0.5	4.8	S
360-375	0.0	3.8	56.7	33.8	1.2	95.5	0.5	4.0	S

Table VIII 3. Extractable bases, acidity, cation exchange capacity, and base saturation of a Candler Typic Quartzipsamment

Depth (cm)	Ca	Mg	Na	K	Sum	Extr acidity	CEC sum	Base sat %
	meq/L							
0-15	0.03	0.02	0.01	0.01	0.07	2.68	2.76	3
30-45	0.03	0.02	0.01	0.01	0.07	1.22	1.29	5
60-75	0.03	0.01	0.01	0.01	0.06	1.43	1.49	4
90-105	0.02	0.02	0.01	0.01	0.06	0.78	0.84	7
120-135	0.02	0.02	0.01	0.00	0.05	1.17	1.22	4
150-165	0.02	0.02	0.01	0.01	0.06	0.03	0.09	67
180-195	0.02	0.01	0.01	0.00	0.04	0.00	0.04	100
210-225	0.03	0.03	0.01	0.01	0.08	0.08	0.16	50
240-255	0.05	0.04	0.01	0.01	0.11	0.42	0.53	21
270-285	0.05	0.04	0.01	0.01	0.11	0.74	0.85	13
300-315	0.04	0.05	0.01	0.01	0.11	0.57	0.68	16
330-345	0.04	0.06	0.01	0.01	0.12	0.56	0.68	18
360-375	0.05	0.07	0.01	0.01	0.14	0.65	0.79	18

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BIOGRAPHICAL SKETCH

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He is married to the former Karen Jones of Glace Bay, Nova Scotia, and they have two sons.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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